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The effect of pH in the synthesis of carbon quantum dots from rice husk on their photoluminescence properties

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Abstract. The dependence of photoluminescence properties to pH solution of carbon quantum dots (CQDs) has been widely investigated. However, the influence of pH condition in synthesis process of CQDs was rarely explored, especially in synthesis by using natural precursor. Herein, this report established the synthesis of CQDs from rice husk by using hydrothermal method in varying pH condition (pH 0-14). The oxidation treatment during synthesis process leads to the initiation of surface defect on carbon precursor. Since surface defect plays crucial role in tuning photoluminescence properties, controlling the amount of oxidant agents was suggested to tune distinct photoluminescence properties. According to High-Resolution Transmission Electron Microscope (HRTEM), pH condition during synthesis affects the size of CQDs which has diameter in the range of 3-20 nm. X-ray Diffractometer (XRD) spectra revealed that the obtained CQDs were amorphous with (002) plane of graphite, while the presence of silica on CQDs was revealed by Energy Dispersive X-ray Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) findings. Photoluminescence spectroscopy showed that the variation of pH in synthesis process broadens the photoluminescence properties of CQDs from green region wavelength to cyan – orange region wavelength (510-632 nm). Therefore, this study suggests that the variation of pH is able to tune photoluminescence properties of CQDs that will be beneficial for its application.

1. Introduction

Carbon quantum dots (CQDs), very small (less than 50 nm) photoluminescent carbon nanoparticles, have been attracted tremendous interest since firstly discovered by Xu, et al. [1], because of its excellent properties, such as facile modification, high solubility, photostability and chemically inert [2]. Afterwards, many studies have been performed to investigate the synthesis process of CQDs from synthetic and natural precursors. Synthesis of CQDs using natural carbon precursor, such as rice husk is preferable due to the low cost and huge supply of precursor. Rice husk is one of major by-product from rice production, which comprises to 20 %wt of paddy rice. In 2016, Malaysia produced 3,492,000 tonnes of paddy rice [3] or approximately 698,400 tonnes of rice husk. Pandey, et al. [4] has synthesized CQDs from rice husk through hot injection method. Hydrothermal method which is simple and low cost was also utilized to synthesis CQDs from oxidized rice husk ash by Wang, et al. [5]. Those methods produced CQDs with green photoluminescence after excitation wavelength at around 400 nm.



Broad and tuneable photoluminescence of CQDs are desired since they are needed for the applications on sensors, bio-imaging, solar cell and photocatalyst [4, 6-8]. Photoluminescence of CQDs depends on its surface defect, which can be tuned through oxidation process on carbon precursor [9, 10]. By controlling the oxygen functional groups on surface of CQDs, different degree of oxidation leads to distinct emission of photoluminescence property. Therefore, this study investigated the influence of pH condition in the synthesis of CQDs from rice husk as carbon precursor by using hydrothermal method on its photoluminescence properties.

2. Materials and method

2.1. Materials

Rice husk were obtained from Jabatan Pertanian Negeri Perak, Malaysia. Nitrogen gas with purity 99.9999% was purchased from Air Products (USA). Nitric acid (HNO₃, 65%) and sodium hydroxide (NaOH pellets, CAS No. 1310-73-2) were purchased from Merck (Germany), while sulphuric acid (H₂SO₄, 95-97%, CAS No. 7664-93-9) was purchased from Qrec (Asia) Sdn. Bhd. These chemicals were employed without further purification or treatment. De-ionized (DI) water (18.2 MΩ) from PureLab Flex was utilized for whole experiment.

2.2. Synthesis carbon quantum dots

CQDs were synthesized from rice husk using hydrothermal method, that has been published in previous study [5] with some modifications.

First, rice husk was washed, dried in oven at 80°C for 6 h, and heated in tube furnace at 700 °C for 2 h under nitrogen atmosphere to obtain rice husk ash. Afterwards, 100 mg of rice husk was oxidized using 10 mL of H₂SO₄ and 3 mL of DI water in water bath sonicator for 5 h, then was continued using 20 mL of HNO₃ for 10 h. The mixture was vacuum-filtered using 0.45 μm membrane and washed using DI water until the pH of filtrate become neutral. The obtained solid residue was then dispersed in 30 mL of DI water and hydrothermally treated in oven at 200 °C for 10 h. CQDs solution was obtained by separating the filtrate using 0.45 μm membrane. After drying process in oven at 60 °C for 1-2 days, the CQDs solution was transformed into powder form.

In this study, CQDs were synthesized without adding functionalization agent and modified the procedure by adding NaOH to vary pH condition from 0 to 14. NaOH was added after introducing HNO₃ in rice husk ash dispersion. CQDs without NaOH addition were labeled as C0; while CQDs with NaOH addition were labeled as C_x, where “x” denoted the pH condition of synthesis process (C2, C4, C7, C10, C14).

2.3. Characterization

The crystallinity of samples was recorded using X-ray Diffractometer on X'Pert3 Powder & Empyrean PANalytical with with Cu Kα irradiation ($\lambda = 1.54$) range of diffraction angles (2θ) from 5 to 80 ° with step size of 2°/step and exposure time of 1s/step. Besides XRD, Raman spectroscopy using Horiba Jobin Yvon HR800 was also used to analyse the crystallinity of samples. Fourier Transform Infrared Spectroscopy (FTIR) and UV-Visible spectra of samples were obtained using Perkin Elmer Spectrum One and Agilent Technologies Cary Series UV-Vis Spectrophotometer, respectively. Imaging of samples was performed using Zeiss Supra55 VP FESEM (Field Emission Scanning Electron Microscopy) and High-Resolution Transmission Electron Microscope (HRTEM) 200 kV with Field Emission, Tecnai G2 20 S-Twin, FEI. Photoluminescence spectra were recorded using Maya2000 Pro Spectrometer with 420 nm excitation wavelength.

3. Result and discussion

3.1. Morphology

Figure 1a and 1b show the morphology and appearance of rice husk ash, respectively. Rice husk ash possesses black color in powder form (figure 1b) and consists of spherical shaped particles in

agglomeration with diameter of ca. 70 nm (figure 1a). Rice husk ash was oxidized and hydrothermally heated to produce CQDs solution, which has transparent color under daylight irradiation (figure 1c) and white powder after drying process (inset of figure 1c). The appearance of rice husk ash and CQDs were similar to study by Wang, et al. [5], which different intrinsic structure between rice husk ash and CQDs was revealed by distinct color of rice husk ash and CQDs.

Different pH condition of oxidation treatment does not affect the appearance of CQDs solution, as shown in figure 1c. However, distinct size of CQDs particles was obtained in different pH condition. The size of C0 was ranging from 6 to 13 nm in diameter. Compared with C0, the diameter of C7 increased to ca. 20 nm; while C14 has lower diameter range than C0, at around to 10 nm. Distinct size of CQDs in various pH conditions is due to the presence of NaOH which has the probability to react with HNO_3 and produce NaNO_3 . Even though NaNO_3 is known as oxidant [11], the ability of NaNO_3 to oxidize might be lower than HNO_3 that results in larger size of C7. After HNO_3 is fully reacted with NaOH (assumed at pH neutral), the excess NaOH acts as oxidant to enhance intercalation process of rice husk ash [12].

The mechanism to alter rice husk ash into CQDs comprises of intercalation and exfoliation processes [13]. Intercalation is started when rice husk ash is dissolved in H_2SO_4 and HNO_3 . Subsequently, washing treatment of rice husk ash with deionized water initiates exfoliation and generate carbon in smaller size particles [14]. The exfoliation processes are supported by HRTEM findings, which the obtained CQDs have smaller size than rice husk ash.

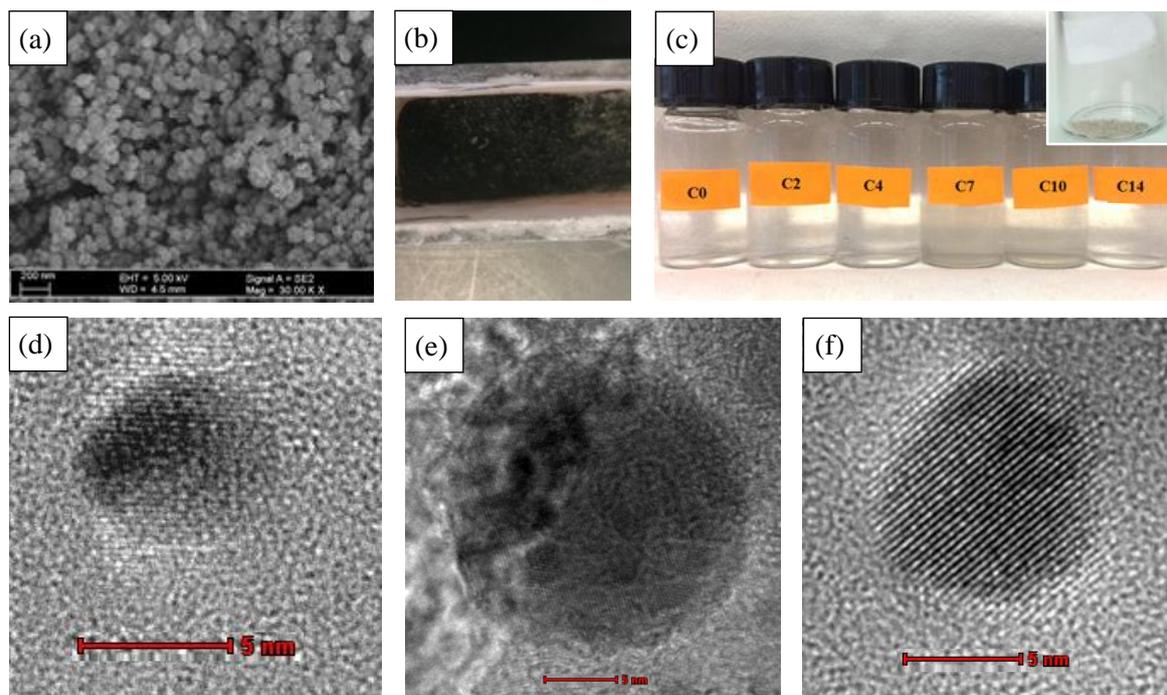


Figure 1. (a) FESEM image and (b) the appearance of rice husk ash; (c) the appearance of CQDs solution samples and inset is CQDs in powder form; HRTEM images of (d) C0, (e) C7 and (f) C14.

Table 1. Diameter and element composition of CQDs samples.

Sampel	Diameter (nm)	Weight %	
		C	Si
C0	6-13	55.85	44.15
C7	~ 20	53.07	46.93
C14	3-10	53.81	46.19

The EDX measurements showed that the obtained CQDs consist of C and Si element with similar weight fraction, as shown in table 1. This finding revealed that both carbon and silica in rice husk were fully utilized in this study, which is in agreement with other studies by Wang, et al. [5] and Pandey, et al. [4] that also synthesized CQDs from rice husk.

3.2. Crystallinity

XRD spectra (figure 2a) depict broad diffraction peaks at 2θ value of ca. 22° that belongs to (002) plane of graphite [15], which indicates CQDs were obtained in amorphous form. The spectra of some samples in different pH condition of synthesis process present the same peaks and intensity. Therefore, pH does not affect the crystallinity profile of CQDs.

Raman spectra as shown in figure 2b provides deeper information on crystallinity of CQDs. Raman spectra that have been fitted using Gauss method (inset of figure 2b), exhibits two peaks centered at ca. 1387 cm^{-1} and ca. 1630 cm^{-1} which attributed to D band and G band of graphitic lattice, respectively [16]. Intensity ratio of D band to G band of C10 was 0.86, which confirmed that the sample has high defect density [8].

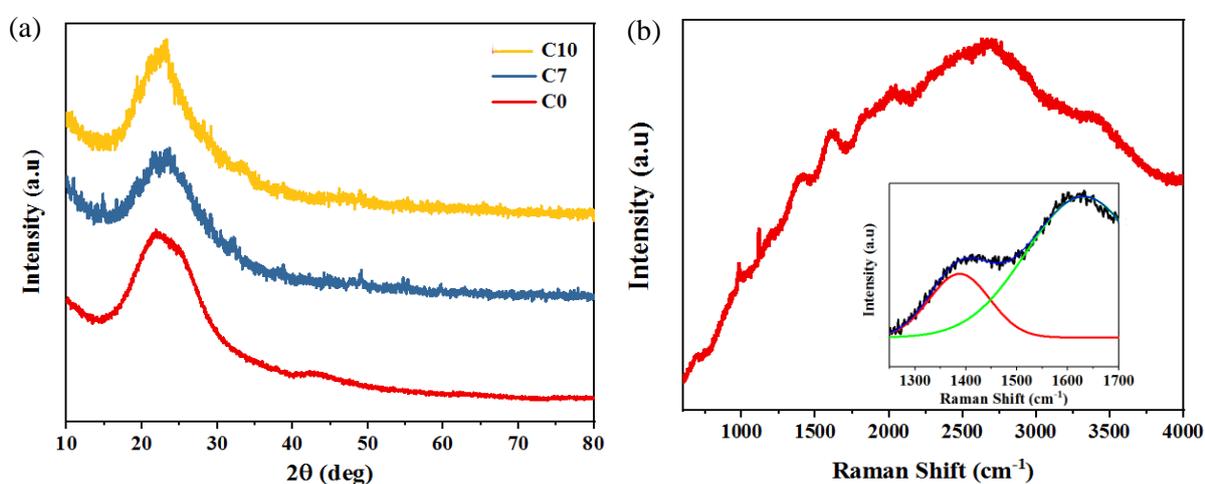


Figure 2. (a) XRD spectra of CQDs samples and (b) Raman spectra of C10 with inset is deconvoluted D and G band using Gauss fit.

3.3. Functional groups on the surface of CQDs

The functional groups on samples were characterized using FTIR spectra (figure 3). Broad peaks around $2900\text{--}3700\text{ cm}^{-1}$ were indicated for --OH bending vibrations on the surface of CQDs. The peaks at 1640 and 1526 cm^{-1} correspond to stretching vibration of C=O [4, 10] and C=C [6, 9], respectively. The stretching vibration of Si-O-C , Si-O-Si , and Si-OH were observed in the range of $950\text{--}1128\text{ cm}^{-1}$ [5]. The presence of oxygen functional group on the surface of CQDs causes CQDs to be perfectly dissolved in water [10] and emit distinct photoluminescence in varying pH of solvent [6, 17].

Inset in figure 3 showed detailed FTIR spectra of samples and revealed that the transmittance of each sample was decreased with the increasing of pH for acid to neutral condition; meanwhile, for neutral to base condition, increased transmittance was recorded. Smaller transmittance of peaks for oxygen functional group indicates lower oxygen content on the surface [10]. Therefore, these findings supported previous assumption in HRTEM analysis, that oxidation process using NaNO_3 was weaker than HNO_3 , and the oxidation became stronger when NaOH is in excess condition.

Even though this study performed similar procedure to previous study by Wang, et al. [5], the obtained samples have slightly different outcomes in functional groups. This might be due to different type of rice husk that used in both study. Each type of rice husk has diverse chemical composition, which depends on climate and characteristic of soil [18].

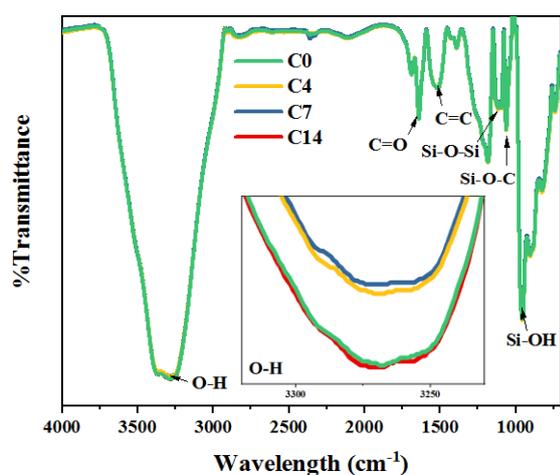


Figure 3. FTIR spectra of CQDs samples and inset is the detailed FTIR spectra for –OH.

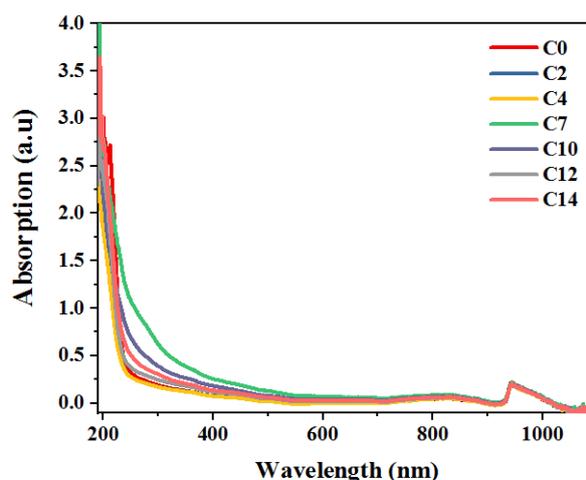


Figure 4. UV-Vis spectra of CQDs samples.

3.4. UV-Vis analysis

As shown in figure 4, the peaks that indicated $\pi \rightarrow \pi^*$ transition were not detected, since these peaks might be located below than 200 nm. However, small hump located at 943 nm possibly indicates the presence of SiO_2 [4]. Furthermore, UV-Vis spectra of samples were slightly shifted in random trends that can be ignored.

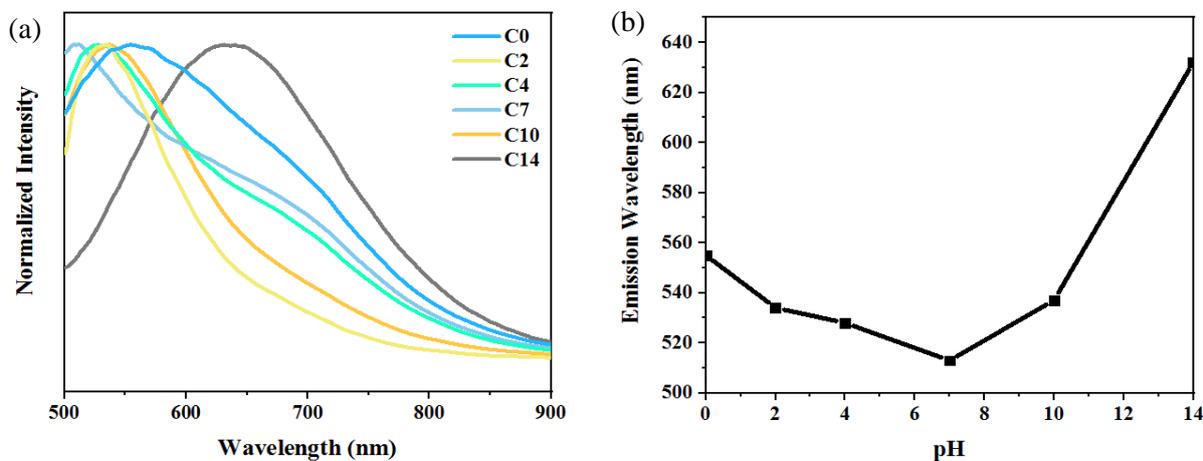


Figure 5. (a) Normalized photoluminescence spectra of CQDs with excitation wavelength of 420 nm and (b) the maximum of emission peak as the function of different pH of synthesis process.

3.5. Photoluminescence analysis

The photoluminescence property of CQDs samples were normalized in intensity to observe the maximum emission wavelength of each sample, as shown in figure 5a. After excitation with 420 nm wavelength, C0, C2, C4, C7, C10 and C14 emitted maximum emission wavelength at 555, 534, 527, 510, 537, and 632 nm, respectively (figure 5b). Similar to Pandey, et al. [4] and Wang, et al. [5], as-prepared CQDs which is C0 emitted green photoluminescence after excitation. The maximum emission wavelength was shifted to shorter wavelength in acidic synthesis process to neutral condition, while neutral to base condition of synthesis process shifted the maximum emission wavelength to larger wavelength. It clearly showed that the maximum emission peak of C14 was sharply increased from green region photoluminescence to orange region photoluminescence. Broad photoluminescence of CQDs is beneficial for its applications, which is potentially applicable in multi-

color imaging that required low toxicity [9] and photocatalyst or solar cells to extend the light absorption that leads to higher performance [2].

The origin of photoluminescence for CQDs has been suggested from: (1) distinct size [17] and (2) surface defect [9, 19] that are caused by oxygen functional group, edge effect, and disorder structure of vacancies [17]. In this study, proportion of the number of oxygen functional groups on the surface (from FTIR findings) and maximum emission wavelength revealed that photoluminescence properties were affected by oxygen functional groups which leads to distinct size of CQDs. In agreement with Jang, et al. [17], the origin of photoluminescence due to the distinct size should include another parameter such as oxygen functional group. Furthermore, similar results for the correlation of oxygen functional group and emitted photoluminescence were suggested by Ding, et al. [9], which higher oxygen functional group on surface leads to the shift of photoluminescence from blue to red region wavelength.

4. Conclusion

This study reported that pH condition in synthesis process is able to tune photoluminescence properties of CQDs from rice husk. Varying pH condition of synthesis process does not affect the crystallinity of samples, but alter the number of oxygen functional groups on the surface and size of the obtained CQDs. According to photoluminescence spectroscopy, varying pH conditions of synthesis process broaden the emission wavelength of CQDs from green photoluminescence to cyan – orange photoluminescence. The origin of photoluminescence in this study was suggested from oxygen functional groups which lead to generation of CQDs in distinct size.

5. References

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