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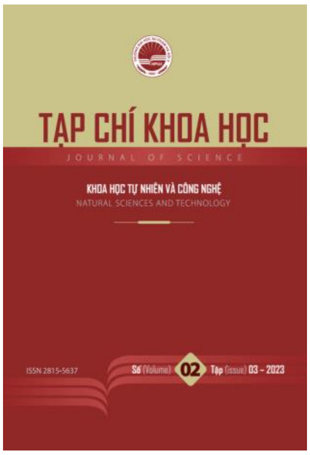

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Control the solubility of carbon quantum dots by solvent engineering

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Abstract

Solubility parameters of carbon quantum dots (CQDs) are important physical properties to deploy CQDs in various applications such as organic light emitting diodes (OLEDs), light-converting materials in LEDs, and photoluminescent sensors for metal ion detection. Because of the low toxicity and tunable emission most CQDs have been designed to be water-soluble and biocompatible; oil-soluble CQDs that are essential for OLEDs are not yet explored. Herein, we used a solvothermal method to prepare CQDs and demonstrated that the solubility of CQDs could be controlled by the synthetic solvent. We used hydrophobic (toluene), ambipolar (ethanol), and polar (water) solvents to prepare three types of CQDs from citric acid and thiourea. Correlating surface chemistry, solubility, and fluorescent properties of the CQDs suggests that the solubility of CQDs is governed by the dominate surface functional groups while the more diversity in the surface functional groups shift the emission of CQDs to longer wavelengths.

Keywords: Carbon quantum dots, solublity parameter, solvent engineering, oil soluble, solvothermal

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1. Introduction

Carbon quantum dots (CQDs) have been emerged as potential materials to replace Cd-based QDs in diverse applications, especially in the fields of biology and biochemistry because CQDs have been improved to be low-toxic, biocompatible, and highly photoluminescent [1], [2]. CQDs could be synthesized by cutting down large C sp^2 structures into nano-sized graphene, known as top-down methods, or by fusing small organic molecules into nano-sized carbogenic dots, known as bottom-up strategy [3]. Solvothermal synthesis has been widely used to prepare CQDs from a large bank of molecular precursors [4]–[7]. Although the concrete formation mechanism of CQDs from molecular precursors is still in discussion the final structure of bottom-up synthetic CQDs could be classified into graphitic dots and carbon nanodots [3]. While graphitic dots exhibits size-dependent absorption and emission spectra [8], [9] the optical properties of carbon nanodots are vastly dominated by a molecular fluorophore which is an intermediate product of the fusion processes [3], [10]. The structure of carbon nanodots is fairly described as a carbogenic dot whose core involves polyaromactic hydrocarbons (PAHs) and the molecular fluorophore [7], [11] while whose surface is decorated with simple groups such as –COOH, –NH_2, and –OH. The optical properties of CQDs are determined by the carbogenic core, surface functional groups, and the chemical bonding between the core and the surface groups. Additionally, the surface functional groups determine the solubility as well as chemical reactivity of CQDs.

From the colloidal chemistry point of view, the solvation of surface functional groups determines the solubility of CQDs in different solvents. In broader sense, the surface functional groups must govern the solubility parameters CQDs. The interactions between the surface functional groups with solvent could lead to the aggregation of CQDs [12], create new emitting centers [13], or redistribute the charge density in the excited states [14] resulting in changes in the photoluminescent properties of CQDs [15]. Additionally, surface functional groups also affect the toxicity [16] and metal ion sensitivity [17] of CQDs. Despite the importance of surface chemistry the surface functional groups of CQDs cannot be exchanged by ligand exchange methods because of the covalent bonding nature in CQDs. Post-surface treatment or tuning the synthetic recipe is necessary to obtain CQDs with target surface functional groups [18]–[21]. Y. Zhang group reported the synthesis of CQDs emitting either in green or red region simply by changing the synthetic solvent from ethylene glycol to glycerol [20]. K. Sahu and co-workers treated solvothermally 1,2,4-triaminobenzene and urea in different solvents to produces CQDs emitting different colors in the visible region [21]. Those early reports imply that solvent engineering could be an important tool for the development of CQDs toward optoelectronic applications where hydrophobic CQDs are necessary.

Herein we used a solvothermal method to prepare CQDs using citric acid and thiourea in different solvents, including toluene, ethanol, and water. Comparing the surface chemistry of CQDs and their optical properties reveals that the emission spectrum of CQDs gets wider as the surface functional groups are more complicated.

2. Experimental section

2.1. Chemicals and facilities

Citric acid monohydrate (CA, 99.8%) and thiourea (TUA, 99.5%) were purchased from Aladdin Chemicals. Ethanol and toluene (HPLC grade) was supplied by Daejung Chemical. Double-distillated water was prepared freshly in the laboratory and used as solvent. A 50 ml, polyparaphenol (PPL) liner autoclave was used as solvothermal reactor. Binder ED115 electric oven was used to provide controlled temperature environment for the solvothermal synthesis.

2.2. The synthesis of carbon quantum dots

1.47 g of CA (7 mmol) and 0.8 g of TUA (10.5 mmol) was dissolved in water and the resultant solution was transferred into a PPL liner autoclave. Solvothermal treatment was carried out in an electric oven at 200°C for 6 hours. After cooling down to room temperature, CQDs was precipitated by adding acetone and collected by centrifugation at 8000 rounds per minute for 10 minutes at 15°C. CQDs were then dispersed in water and filtered using a 0.22 µm syringe filter to remove large particles. Toluene and ethanol was used instead of water to obtain tol-CQDs and eth-CQDs, respectively.

2.3. Characterizations

The absorption spectra CQDs were carried out using an UV-2450 (Shimadzu) spectrometer while photoluminescent (PL) and photoluminescent excitation spectra (PLE) were conducted on FLS1000 (Edinburgh Instrument) fluorescent spectrometer. Jasco FT/IR6300 spectrometer was used to measure FTIR spectra of CQDs.

3. Results and discussion

In a previous study, we were successful in preparation of CQDs from CA and TUA in acetone by a solvothermal method; the diameter of CQDs varied from 2.5 to 8.5 nm [6]. In current study, we explored the solvothermal method to different solvents, including toluene, ethanol, and water. The formation of CQDs could be indirectly improved by the photoluminescence of the CQDs dissolved in the mother solvents as shown in picture a)-c) in Fig. 1.

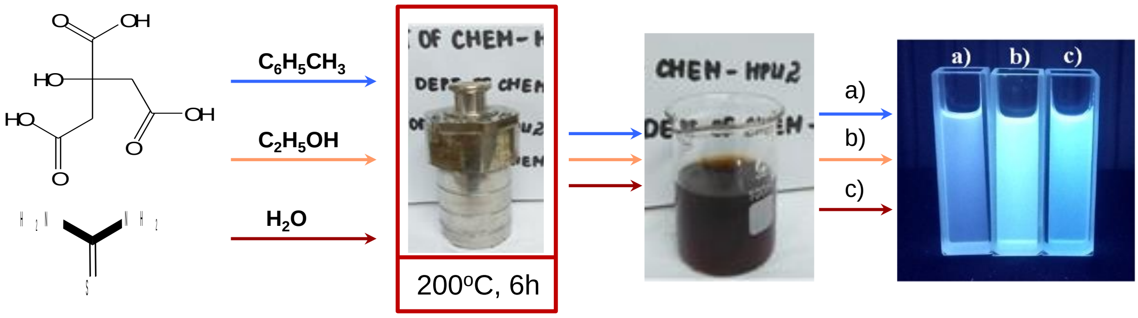

Figure 1. Step-wise synthesis of carbon quantum dots. Solutions of tol-CQDs (a), eth-CQDs (b), and wat-CQDs (c) under UV light at 365 nm.

Table 1. Solubility of CQDs in different solvents

Solvents:	**hexane**	**toluene**	**chlorobenzene**	**chloroform**	**acetonitrile**	**ethanol**	**methanol**	**Water**
tol-CQDs	S	S	S	S	I	I	I	I
eth-CQDs	I	S	S	S	S	S	S	S
wat-CQDs	I	I	I	I	S	I	S	S

S: soluble; I: insoluble

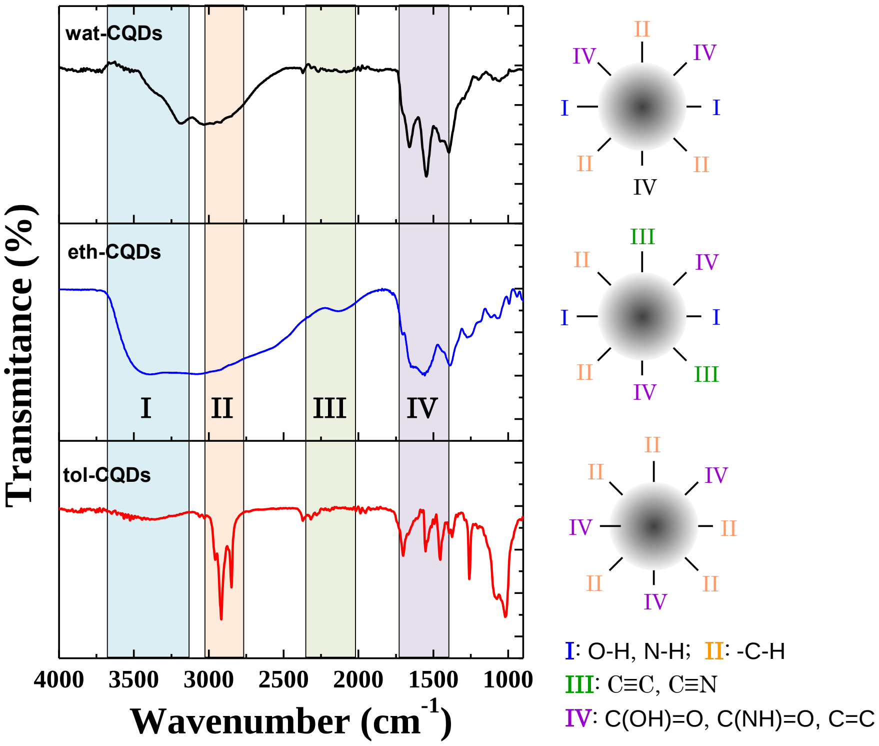

Figure 2. FTIR spectra of CQDs prepared by a solvothermal method using toluene (tol-), ethanol (eth), and water (wat) solvents. I, II, III, and IV are four groups bonds recognized by the FTIR spectra.

The solubility of CQDs indifferent solvents was tested simply by dissolving about 20 mg into 2 ml of the solvent; CQDs was sad to soluble in a solvent if a homogeneous solution was obtained. The solubility of CQDs is given in Table 1. Wat-CQDs are soluble in protic or highly polar solvents such as acetonitrile, methanol, and water; Tol-CQDs are soluble in nonpolar solvent such as hexane, toluene, and chlorobenzene while eth-CQDs are soluble in various solvents. To correlate the solubility of CQDs with their surface chemistry we conducted Fourier transform infrared (FTIR) spectra of dried CQDs and the results are summarized in Fig. 2. We selected four important vibrational regions into consideration which are noted as I, II, III, and IV respectively in Fig. 2. Stretching vibrations of polar O-H or N-S bonds appear in region I while stretching of aliphatic C-H bonds is observed in region II. Possible triple bonds such as C≡C or C≡N would be found in region III. C=O bonds either in carboxylic acid, ester, and amide and C=C bonds are visible in region IV [6], [18], [22], [23]. The results indicate that tol-CQDs involve types I and IV functional groups; wat-CQDs include types I, II, and IV while eth-CQDs include all types as modeled in Fig. 2. The existence of functional groups with different polarities on the surface of CQDs is in line with the solubility of CQDs in Table 1.

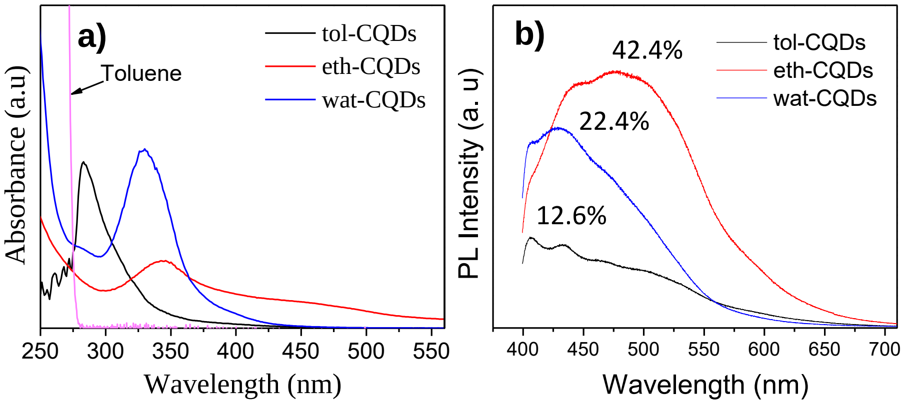

Figure 3. a) absorption and **b**) photoluminescent spectra of CQDs prepared in toluene (tol-), ethanol (eth-), and water (wat-). The relative quantum emission efficiencies are given in **b**).

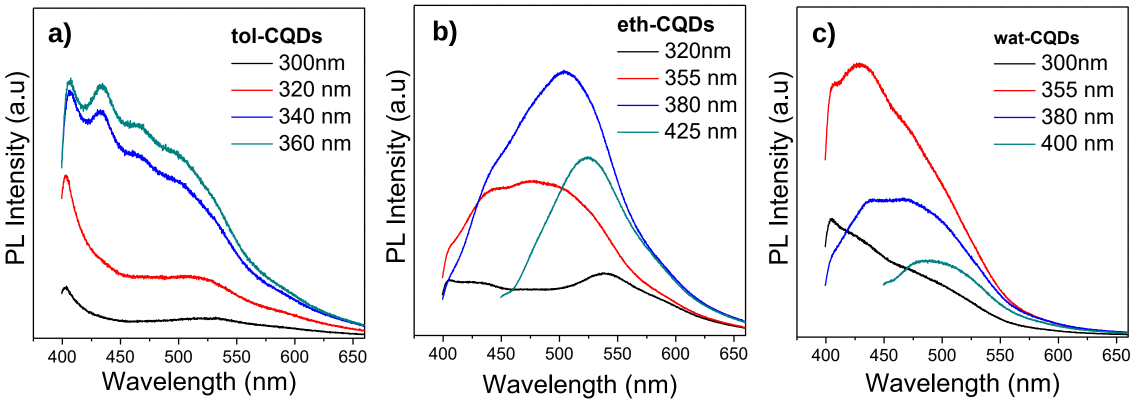

Figure 4. Excitation-dependent photoluminescent spectra of CQDs prepared in toluene (tol-), ethanol (eth-), and water (wat-).

The optical properties of CQDs are summarized in Fig. 3 and Fig. 4. The absorption of tol-CQDs dissolved in toluene was featureless; an absorption tail whose absorbance decreased gradually with the wavelength was similar to the absorption profile of graphene oxide [24]. The observed absorption band at 280 nm was likely due to the subtraction absorbance of sample to that of toluene solvent. Eth-CQDs and wat-CQDs exhibited an absorption band at 330-340 nm which could be assigned to an molecular fluorophore formed via the condensation between CA and TUA [3]. Compared to other CQDs, eth-CQDs had significant absorbance above 400 nm which originates from low-energy states of surface functional groups [10]. This difference was consistent with the FTIR results discussed above that eth-CQDs possessed much richer surface functional groups than other CQDs. The photoluminescent spectra of CQDs are shown in Fig. 3b. While the emission spectra of tol-CQDs and wat-CQDs were mostly in the deep blue region maximized at about 425 nm the emission spectrum of eth-CQDs shifted to blue-green region, maximized at 480 nm. The emission quantum yield that was calculated by compared to quinine sulfate increased in the order of tol-CQDs (12.6%), wat-CQDs (22.4%), and eth-CQDs (42.4%). Likely, the more surface sates provide more luminescent recombination channels in CQDs. To study further into the emission mechanism of CQDs, we measured PL spectra of CQDs by varying the excitation wavelength across the absorption range of CQDs; the results are shown in Fig. 4. When changing the excitation wavelength, the emission spectrum of tol-CQDs only changed in the relative intensity. The PL maximum of wat-CQDs shifted gradually from 425 nm to 500 nm when increasing the excitation wavelength from 300 nm to 400 nm.

In the case of eth-CQDs, a new emitting center was unrevealed at 530 nm and it was clearly observed when being excited in the low-energy surface states (>400 nm), Fig. 4b.

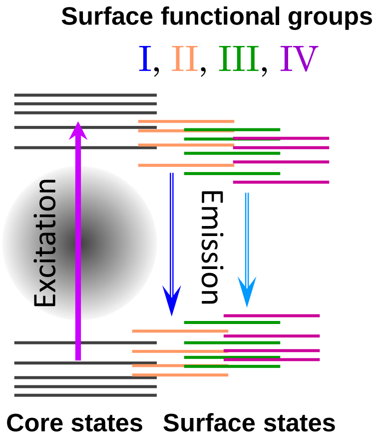

Figure 5. Proposed electronic structures of carbon quantum dots having different surface functional groups

To explain the optical properties of CQDs, we put forward a tentative model in Fig. 5. Solvothermal synthesized CQDs were reasonably modelled as carbogenic dots which included PAHs and molecular fluorophores in the core and functional groups on the surfaces; the model have been widely used in bottom-up synthesized CQDs [3], [10]. Because of the covalent bonding nature in CQDs, the surface functional groups add electronic states to the whole CQDs. The electronic states whose energy is lower than that of core states could provide luminescent recombination channels in CQDs. The existence of such low-energy states is indicated by the absorbance of CQDs in long-wavelength regions [10] as seen in eth-CQDs in Fig. 3a. The larger diversity in surface functional groups gives the more density of low-energy states that leads to red-shift in the emission spectrum and increase in emission efficiency. This explains why eth-CQDs had a higher quantum yield and emitted more efficiently in the longer-wavelength regions (Fig. 3b).

4. Conclusions

Three types of CQDs with controlled solubility were successfully prepared by changing the synthetic solvent used in a solvothermal method. The surface of CQDs is more hydrophobic if they are synthesized in toluene and vice versa, the surface is more hydrophilic if the CQDs are synthesized in water. The surface chemistry of CQDs is the most diverse when CQDs are prepared in an amphiphilic solvents such as ethanol. A diversity in the surface functional groups of CQDs leads to more light absorption and emission in the longer-wavelength regions. The results demonstrated herein offer a way to prepare oil-soluble CQDs for optoelectronic applications and suggest that solvent engineering is an efficient tool for tuning the optical properties of CQDs.

Declaration of Competing Interest

The authors declare no competing interests.

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