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Synthesis and Characterization of Dried Leaves Derived Carbon Quantum Dots and g-C₃N₄ Composite

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Abstract. In this work, carbon quantum dots (CDs) was successfully synthesized by hydrothermal treatment using dried leaves as green precursor. Graphitic carbon nitride (g-C₃N₄) was combined with CDs to prepare CDs/g-C₃N₄ composites with three different weight percentage at 0.6, 0.8 and 1.0 wt%, respectively. The morphological structure, optical properties and chemical compositions of CDs and composites were characterized using various spectroscopic techniques. CDs solution portrayed a significant fluorescence property that bright blue-green fluorescence can be observed by naked eye under ultraviolet (UV) light irradiation. The highest fluorescence emission was recorded at 320 nm with the optimal excitation wavelength of 423 nm. Ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) results displayed red-shifted adsorption spectra of CDs/g-C₃N₄ composites from 500 nm to 800 nm. No upconversion photoluminescence (UCPL) was detected in CDs based on the photoluminescence (PL) study. The loading of CDs on g-C₃N₄ reduced the band gap from 2.7 eV to 2.59 eV.

1. Introduction

In the early of 21st century, carbon quantum dots (CQDs) were first discovered in a research for purification of fluorescent single-walled nanotubes (SWNTs) [1] whereby it was later on widely known as carbon dots (CDs). In general, CDs are semiconductor nanoparticles with the diameter size of less than 10 nm [2] that composed of graphitic carbon (sp²-hybridization) and contributed to quantum confinement effect. With this discovery, CDs and graphene quantum dots (GQDs) which both have the similar structural properties were getting significant interest and attention in nanotechnology and scientific field. This is due to their distinct advantages in terms of properties such as low toxicity [3], tuneable and comparable photoluminescence (PL) [4] chemical stability [5], and a wide range selection of environmental friendly synthesis process [2]. In recent years, hydrothermal method is widely used to produce CDs because this method is low toxicity, controllable size, can be prepared in the large amount, ability to recycle waste and safe. The CDs were prepared through hydrothermal treatment by using different precursors such as orange juice, strawberry juice, grass, waste paper, and other chemicals. The hydrothermal treatment of CDs usually involves the use of biomaterials, waste and less hazardous precursor and thus it is more environmentally friendly.



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Hydrothermal is the term that refers to any heterogeneous chemical reaction in the presence of an aqueous or non-aqueous solvent above room temperature and greater than atmospheric pressure in a closed system [6]. Hydrothermal method is chosen to produce high quantum yield CDs by using low level of oxygen heating. Moreover, the reaction times are reduced with a good control of the crystallization, crystal size, purity and morphology of the products. The g-C₃N₄ was widely used in photoluminescence applications such as photodegradation of Rhodamine B and methyl orange, activation of dioxygen and converting CO₂ to fuel. In the domain of photocatalytic application, g-C₃N₄ tend to produce lower quantum efficiency that is about 1 % at 420 nm due to its fast electron charge recombination and poor conductivity [7]. Instead of using titanium dioxide (TiO₂) that had been widely chosen as one of the promising semiconductor in heterogeneous photocatalysis, g-C₃N₄ dominates TiO₂ since it is more economical, high thermal and chemical stability and better visible absorption properties and a greener semiconductor selection without the use of metal. The low quantum efficiency of g-C₃N₄ in photocatalytic application can be solved by incorporating highly photoluminescent CDs into the g-C₃N₄ to form hybridized CDs/g-C₃N₄.

2. Materials and methods

2.1. Preparation of CDs solution

Dried Bucida (*Buccida Buceras*), Kelat Paya (*Eugenia Oleina*), Indian Rosewood (*Dalbergia Latifolia*) and Hop Tree (*Arfeuillea Arborescens*) leaves were obtained from Universiti Tunku Abdul Rahman, Kampar campus, Malaysia. These leaves were dried in the oven for 12 h at 120 °C. 5 g of the leaves were mixed with 100 mL of ultrapure water in a 150 mL Teflon-lined stainless steel autoclave for 12 h at 200 °C. The dark brown solution was centrifuged for 20 min at 5,000 rpm to separate the large particles from the solution.

2.2. Preparation of CDs/g-C₃N₄

Pure g-C₃N₄ was prepared by putting urea (Merck, 99%) into an alumina crucible with lid and heated in muffle furnace at 550 °C for 3 h. The yellowish product, g-C₃N₄ (0.1 g) was then mixed with 1 mg/mL of CDs solution and heated at 100 °C for 2 h in Teflon-lined stainless steel autoclave. The obtained product was centrifuged at 5000 rpm for 15 min and washed with deionized water for several times. It was then dried at 60 °C overnight. By following the same procedure, the composites of CDs/g-C₃N₄ with different amount of CDs (0.6, 0.8, 1.0 wt%) were prepared and denoted as CDs/g-C₃N₄-0.6, CDs/g-C₃N₄-0.8, and CDs/g-C₃N₄-1.0, respectively.

2.3. Characterization of CDs/g-C₃N₄

The morphological and elemental information were determined by using field emission scanning electron microscopy (FESEM, JEOL 6701-F) and energy dispersive X-ray spectroscopy (EDX). The photoluminescence (PL) spectra of CDs solution were acquired with a PL spectrophotometer (Perkin Elmer LS 55). The ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) was obtained using Shimadzu UV-2600 spectrophotometer equipped with integrating sphere attachment with BaSO₄ as a reference.

3. Results and discussion

3.1. FESEM and EDX

FESEM was carried out to identify the morphology and structure of CDs, g-C₃N₄ and CDs/g-C₃N₄ composites. Figure 1(a) shows the FESEM image of CDs which observed to have irregular shapes with the particles size distribution ranging from 1 μm to 2.86 μm. FESEM image of g-C₃N₄ in figure 1(b) illustrate the shape of g-C₃N₄ to be irregular crumpled lamellar structure. In figure 1(c-e), it clearly shows that wrinkled structure of g-C₃N₄ provided a better support for the attachment of CDs at different concentration where higher concentration CDs/g-C₃N₄ composite exhibited a more packed and aggregated morphological structure. In order to identify the elemental composition of CDs/g-C₃N₄ composites, EDX was carried out to confirm the presence of carbon (C), nitrogen (N) and oxygen (O)

in CDs/g-C₃N₄-0.8 composite. The weight percentage of C, N and O were found to be 37.13, 57.45 and 5.42 %. The C and N elements originate from g-C₃N₄ while O element was contributed by the reaction between urea and oxygen during the preparation of g-C₃N₄.

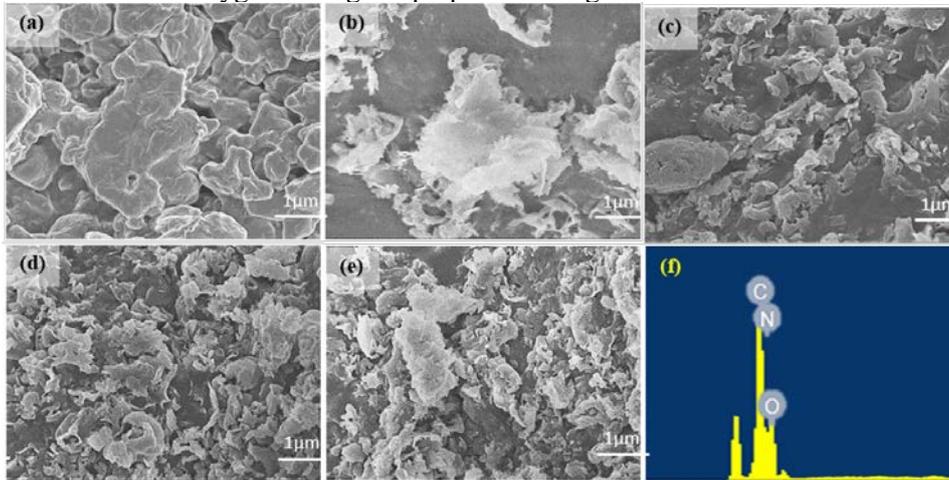


Figure 1. FESEM images of (a) CDs; (b) g-C₃N₄; (c) CDs/g-C₃N₄-0.6; (d) CDs/g-C₃N₄-0.8; (e) CDs/g-C₃N₄-1.0; and (f) EDX of CDs/g-C₃N₄-0.8.

3.2. Optical properties

Optical properties of CDs are considered one of the crucial factor that will affect the applications of CDs. The colour of CDs solution under daylight is brown as shown in the inset of figure 2. The CDs solution shows a bright blue-green fluorescence colour under the irradiation of ultraviolet (UV) light. The blue-green fluorescence of CDs that can be observed by naked eye visually confirmed its fluorescence characteristic that renders it a promising candidate in broad range of applications [8]. Figure 2 shows the UV-vis absorption spectrum of CDs solution in the range of 200 nm to 800 nm. There is only one absorption peaks at 303 nm which is attributed to n-π* transition of C=O bonds in CDs [9].

Figure 3 illustrates the photoluminescence (PL) emission spectra behaviour across the excitation wavelength ranging from 300 nm to 500 nm. The excitation wavelength at 320 nm recorded the optimal emission wavelength at 423 nm. When the excitation wavelength increases, the emission spectrum are red-shifted to higher wavelengths with lower emission intensity. These observations are consistent with the previous reports [10, 11]. Although the origin of PL luminescence in CDs is not fully clarified, the excitation-dependent PL behaviour could be interrelated to the different size distribution of CDs, multiple distribution of emissive site on passivated CDs and photogenerated charges recombination at surface-confined defect states [12, 13, 14]. Besides, there is no emission peak beyond the excitation wavelength of 500 nm, showing the absence of upconversion photoluminescence (UCPL) properties in CDs. In order for UCPL to occur, multiphotons must be activated simultaneously by absorbing two or more photons at the same time which emission wavelength emitted is shorter than the excitation wavelength [15]. Previous study reported that most of the CDs did not possess upconversion fluorescence. The detected UCPL properties actually originated from normal fluorescence excited by leaking component from second diffraction in the monochromator of the fluorescence spectrophotometer [16].

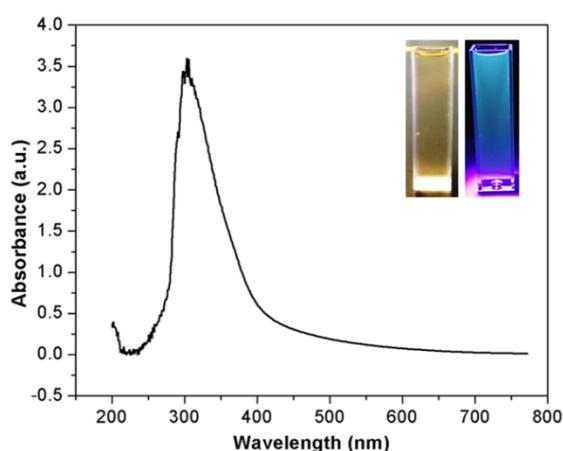


Figure 2. The UV-vis absorption spectrum of CDs solution. Inset shows the fluorescence of CDs solutions under daylight (left) and UV light (right).

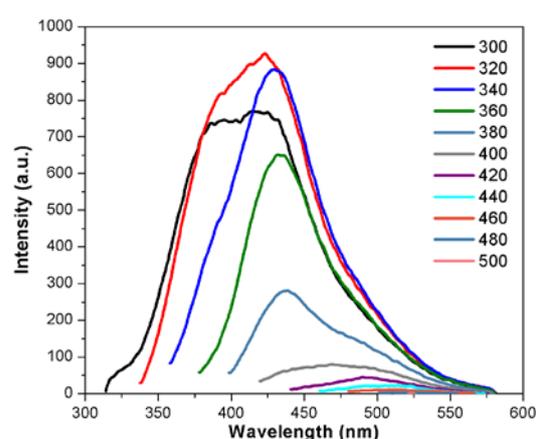


Figure 3. Photoluminescence emission wavelength of CDs solution at different excitation spectrum.

The study of ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) is shown in figure 4(a). The absorption spectra for all CDs/g- C_3N_4 composites is blue-shifted towards UV region before the cut-off wavelength at 450 nm but the absorption spectra start to red-shift towards visible region after 450 nm. The band gap of photocatalyst can be determined using Tauc plot where $(F(R) \cdot hv)^{1/2}$ was plotted against photon energy, hv as shown in figure 4(b). The band gap of each photocatalysts is obtained from x-intercept by drawing a tangent line of each curve. The band gap for g- C_3N_4 is 2.70 eV while the band gap for CDs/g- C_3N_4 -0.6, CDs/g- C_3N_4 -0.8, and CDs/g- C_3N_4 -1.0 composites is 2.68 eV, 2.65 eV and 2.59 eV, respectively. This results indicate that the increase of CDs weight percentage in the composite will lead to the reduction of band gap energy for improved visible light absorption. It is summarized that the light harvesting capability of photocatalysts follows the sequence of CDs/g- C_3N_4 -1.0 > CDs/g- C_3N_4 -0.8 > CDs/g- C_3N_4 -0.6 > g- C_3N_4 .

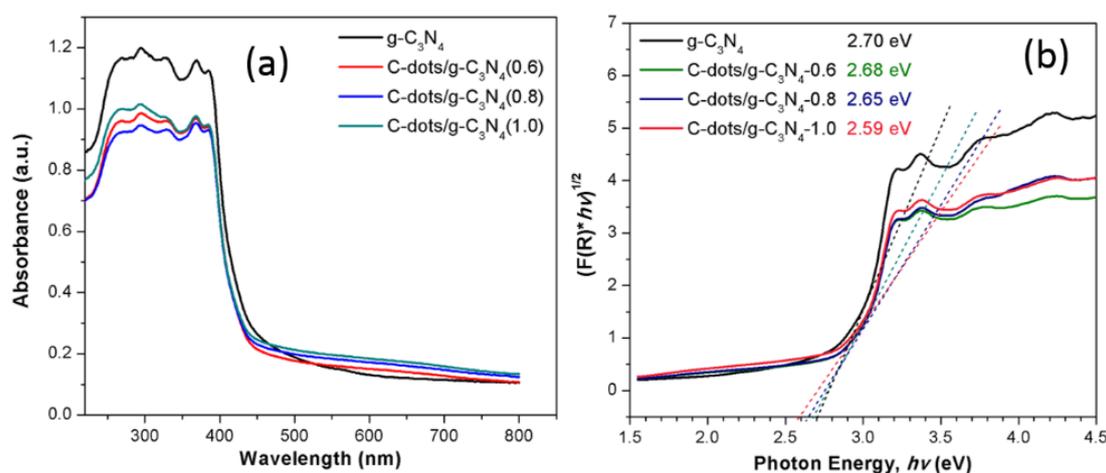


Figure 4. (a) UV-visible diffuse reflectance spectra of g- C_3N_4 , CDs/g- C_3N_4 -0.6, CDs/g- C_3N_4 -0.8, and CDs/g- C_3N_4 -1.0; (b) Tauc plots of g- C_3N_4 , CDs/g- C_3N_4 -0.6, CDs/g- C_3N_4 -0.8, and CDs/g- C_3N_4 -1.0.

4. Conclusions

CDs were successfully synthesized by using dried leaves as starting material through hydrothermal treatment. The PL emission spectra indicated the optimal emission wavelength of CDs at 423 nm upon excitation at 320 nm wavelength. The UCPL properties was not observed in all CDs/g- C_3N_4

composites. All CDs/g-C₃N₄ composites displayed the extension of light absorption range towards visible and NIR region from 500 nm to 800 nm. No upconversion photoluminescence (UCPL) was detected in CDs based on the photoluminescence (PL) study. The band gap energy was reduced from 2.7 eV to 2.59 eV after loading 1 wt% of CDs onto g-C₃N₄. Overall, the preparation of CDs/g-C₃N₄ composites are considered cost effective and environmentally friendly as no harmful chemicals had been used and dried leaves is a green precursor.

Acknowledgments

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