

Tunable carbon quantum dots from starch via microwave assisted carbonization

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Abstract

Tunable luminescence carbon dots (C-dots) were prepared through microwave-assisted carbonization of aqueous starch suspension mediated by sulfuric and phosphoric acids respectively as surface passivating agents. The as-prepared C-dots showed green, blue and yellow luminescence under 365nm UV light. The C-dots were further characterized by UV-Vis, FTIR, and band gap determination. Fourier transform infrared spectroscopy (FTIR) studies revealed bands at 3460 cm^{-1} (OH), 2979 cm^{-1} 1708 cm^{-1} (C=O), 1188 and 1040 cm^{-1} (C-O), and 1397 cm^{-1} (C=C) indicative of the graphitic nature of the carbon. The UV-Vis showed blue shifted absorption bands, while the band gap calculated revealed narrow sizing of the C-dots in the semiconductor range. The results suggest that this approach may serve as a facile route to colour tunable photoluminescent C-dot materials with potential biological applications.

Keywords: Carbon quantum dots, Semiconductor, Starch, Microwave, Luminescence

1. Introduction

Carbon dots (C-dots) like other elemental quantum dots (Q-dots) [1] are semiconductor nanocrystals in the size range of 1 to 10 nm. These nanoparticles have size-selective luminescence properties due to their quantum confinement effect and are currently finding increasing interest in optoelectronics, bio sensing, bio imaging and medicine [2]. Unfortunately, many of the useful (Q-dots) are of highly toxic elemental composition [2, 3].

Carbon-based quantum dots (CQDs or C-dots) are trending as new candidates due to their good solubility and unique optical properties [4, 5], exceptional biocompatibility [3], easy functionalization and their potential as drug delivery vehicles [6] amongst others. All these confer C-dots the edge over metallic semiconductor Q-dots such as CdTe, CdS and PbS [7-10]. Synthetic strategy to obtain C-dots include ‘top-down’ approaches like electrochemical etching, lithography and laser ablation [11–14] etc., and ‘bottom-up’ protocols such as hydrothermal, pyrolytic and microwave carbonization methods [15–18].

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Biogenic precursors to C-dots have included sources such as orange juice [16], by thermal processing of bread, caramel, corn flakes and biscuits [19], hydrothermal treatment

Microwave assisted synthesis is a rapid approach that has been utilized for mostly blue luminescence [22-25] and fewer for other colours [26-27] of C-dots. It is therefore our objective of this study is to explore a facile approach to obtain C-dots with tunable photoluminescence (blue, green and yellow) colours. The precursor starch were extracted from four different raw carbohydrate food sources and thereafter carbonized through microwave-assisted treatment in the presence of either sulfuric or phosphoric acids respectively as surface passivating agents.

2. Materials and Methods

2.1 Materials

Carbohydrate sources for starch were; cassava (*Manihot esculenta*), potato (*Solanum tuberosum*), yam (*Dioscorea rotundata*) and rice (*Oryza sativa*). Other reagents include sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) (Sigma-Aldrich), sodium hydroxide (NaOH) (BDH) and deionized water. A domestic microwave oven with (2.0 cm) diameter hole drilled into the top.

2.2 Extraction of Starch

Starch was extracted from potato, cassava, rice and yam respectively. In a typical procedure, cassava and yam tubers or potato were peeled, grated and soaked in deionized water for 1hr. Each of the resulting mixtures was stirred and then filtered using cheesecloth to obtain starch suspension that was allowed to stand for 2-3hrs. The supernatant was decanted and the bottom residue air dried to obtain the corresponding powdered starch.

Separately, rice starch was obtained by initially pulverizing rice grains to coarse powder using a mortar and pestle. Thereafter, twice the volume of water was added and allowed to soak for about 2 hrs. The mixture was filtered using cheesecloth and further treated as described above to give the dried rice starch powder.

The obtained potato, cassava, yam and rice starch powders were used as precursors for C-dot synthesis.

2.3 Microwave Synthesis of Carbon Dots (C-dots)

C-dots were prepared through microwave assisted carbonization of the starch suspensions in water. In a typical procedure, cassava starch powder (1g) was dispersed in 25ml of deionized water in a beaker to give a suspension. Sulphuric acid (7.0 ml, 2M) was added to the starch suspension followed by carbonization under microwave energy at 500W for 3-7 minutes. The colour of the mixture changed progressively from white through light brown and finally to dark brown. The resulting final dark brown mixture was filtered to give a clear filtrate that was kept for further analysis.

Additionally, fresh cassava starch was carbonized after addition of 3.0 ml concentrated phosphoric acid (14.6M) as the surface passivating agent. The reaction mixture also showed similar progressive colour transformation. The final dark mixture obtained was filtered to give a clear filtrate that was kept for further analysis.

Rice, potato and yam starches were variously carbonized through similar procedures after addition of sulphuric acid (H_2SO_4) or phosphoric acid (H_3PO_4) as surface passivating

agents. The heating regimes were slightly modified to facilitate green and yellow luminescence colours as shown in Table 1. For example, in order to obtain yellow colour with phosphoric acid (H_3PO_4) acid, the carbonization was carried out at 70W-150W for 30-60 minutes. After the colour of the suspension turned to brown, it was then neutralized with 4ml NaOH (5M) solution, before filtration to give a clear solution which was kept for further analysis.

2.4 Characterization of C-Dots

The prepared C-dots were characterized with ultraviolet-visible spectroscopy (UV-Vis) on a T80⁺ UV-Vis spectrophotometer in the range 200 – 900 nm using distilled water for base line correction. Fourier Transform Infrared spectra (FTIR) were recorded on a BRUKER (vector 22) spectrophotometer over the range of approximately 4000-400 cm^{-1} . Optical band gap were calculated from cut off wavelength values obtained from UV-Vis absorption spectra using the equation below:

$$\text{Band Gap Energy; } (E) = h \times c / \lambda \quad (1)$$

Where E (band gap energy), h (Planck's constant), c (speed of light) and λ (cut off wavelength).

The luminescence characteristics of the aqueous filtrates obtained from the carbonization step were investigated by illumination under (365nm) ultra violet (UV) light source in a dark room.

3. Results and Discussion

3.1 Extraction of Starch

The raw carbohydrate food stuffs; potato, cassava, rice and yam utilized in this study as precursor carbon sources are shown in Fig. 1(a-d). Starch powders (Fig. 2a-d) were obtained after processing of the food stuff through peeling, grating (or pulverizing), soaking, filtering, decanting of the supernatant and finally drying of the bottom residue.

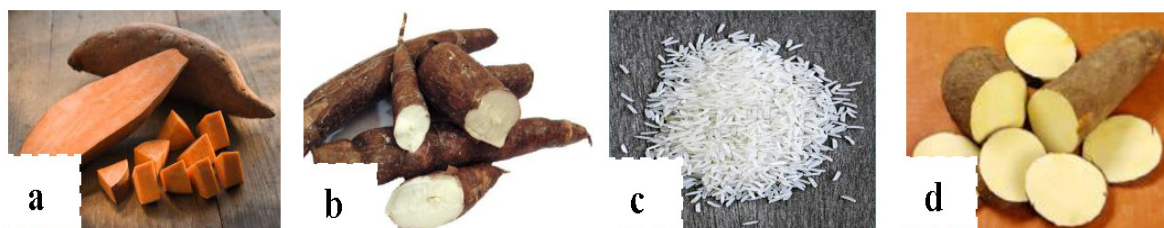


Fig.1: Raw carbohydrate food sources; (a) Potato, (b) Cassava, (c) Rice and (d) Yam.

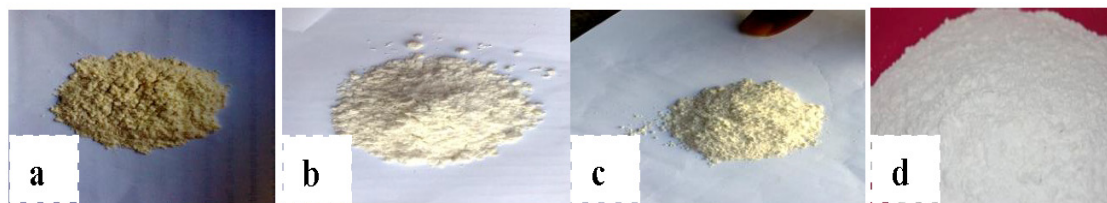
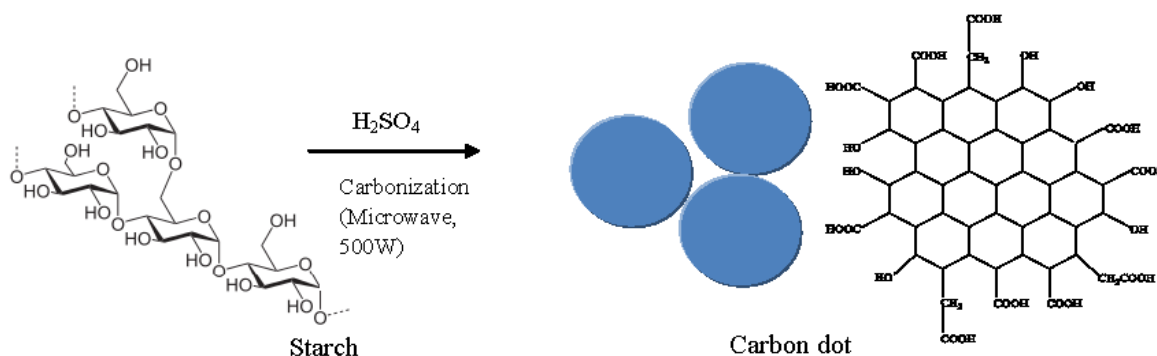


Fig. 2: Starch obtained from; (a) Potato, (b) Cassava, (c) Rice, and (d) Yam.

3.2 Synthesis of C-Dots

The pathway for C-dots synthesis shown in Scheme 1 from the precursor starch is mediated by either H_2SO_4 or H_3PO_4 as surface passivating agents under microwave energy carbonization. The reaction mixture changes from white through light brown and finally to dark brown (Fig 3a-b) to give the filtrate (Fig. 3c). It is envisioned that the starch moiety undergoes hydrolysis to form glucose and fructose which are dehydrated to furfural intermediates and smaller fragmented molecules [28-29]. The intermediates formed then polymerize or aromatize into soluble polymers and aromatic clusters. Furthermore, intermolecular dehydration of the smaller molecules or separation of the aromatic clusters after reaching supersaturation [30-32] facilitates nucleation of the C-dots. Additionally, oxidation introduces functional groups that enhance their water solubility [33].



Scheme 1: Synthesis of C-dots from starch.

3.3 Optical Study of the C-Dots

The luminescence properties of the as prepared C-dots solutions were investigated by irradiation with 365nm UV light. The representative colour in normal light is shown in Fig. 4a, while the characteristic blue, green and yellow luminescence colours are shown in Fig.4b-d. Modification of carbonization protocol on the luminescence characteristics of the C-dots were investigated and presumed to be a function of the heating (wattage), time and the surface passivating agent as highlighted on Table 1.

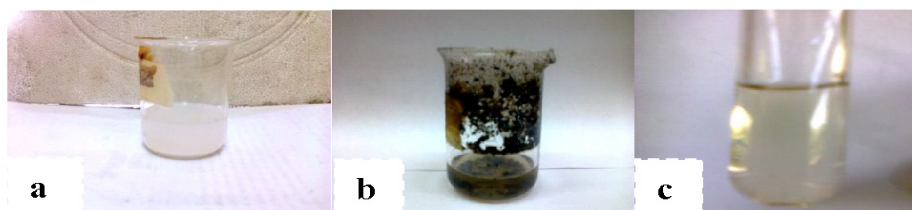


Fig. 3: (a) Starch suspension (b) after microwave carbonization (c) solution after filtration.

Sulphuric acid mediated carbonization at 500 W for 3-5 minutes or 5-10 minutes affords blue- or the green-emitting C-dots respectively. It is interesting to note that yellow colour was only obtained by carbonization at lower temperature (70-150 W) albeit for a longer time (30-60 minutes) using phosphoric acid as passivating agent. In this instance however, the reaction mixture is neutralized with a base. The reaction mixture actually showed no luminescence prior to neutralization with NaOH.

Consequently, the ability to tune the observed emission colours of the C-dots and their good solubility are desirable characteristics for quantum-dot based candidate probes in biological applications.

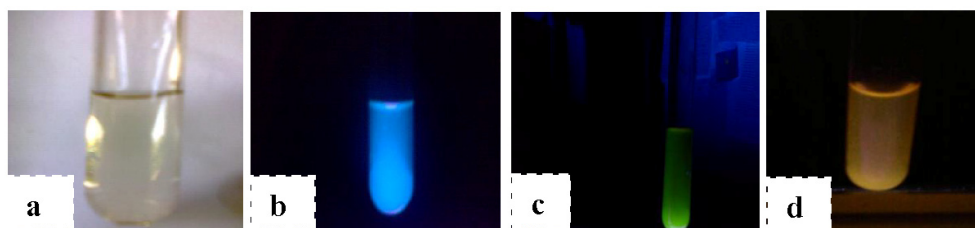


Fig. 4: C-dot solutions; (a) under normal light. Under 365 nm UV excitation; (b) blue, (c) green and (d) yellow.

3.4 Fourier Infrared Spectroscopy (FTIR)

The as prepared C-dots were investigated with FTIR spectroscopy particularly to evaluate the functional groups that decorate their edges. In the representative spectrum shown in Fig.5, there is a broad peak centered at 3460cm^{-1} characteristic of the stretching vibrations of a hydroxyl hydrogen bonded O-H. Peaks at 2979cm^{-1} and 1397cm^{-1} indicate the presence of C-H stretching and C=C stretching vibrations indicative of the graphitic nature of the C-dots [34-35]. The broad peak at 2555cm^{-1} and the strong sharp absorption peak observed at 1708cm^{-1} is associated with O-H and C=O stretching vibrations of carboxyl group. Additionally, there were peaks at 1188 and 1040cm^{-1} assigned to C-O stretching vibrations of carboxyl and hydroxyl groups respectively. The functional groups identified from FTIR analysis corroborate the hydrophilicity and solubility of the C-dots in water.

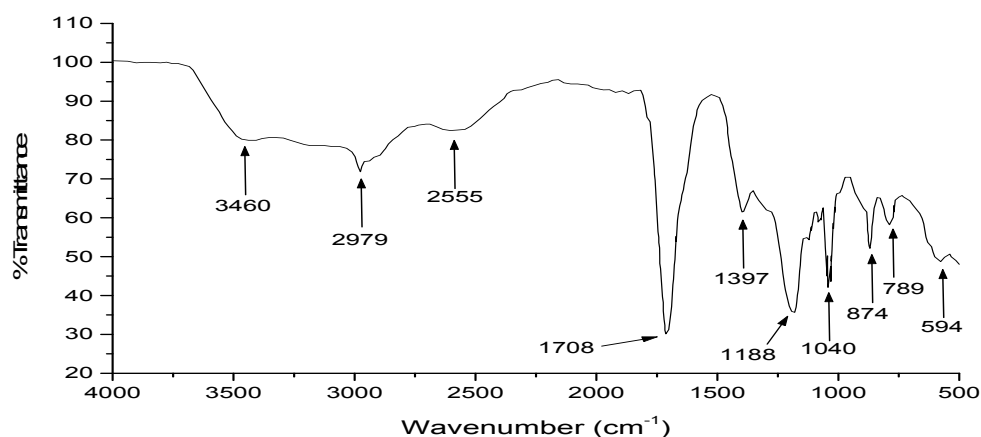


Fig. 5: Infrared spectrum of C-dot

3.5 UV-Vis Absorption Spectra of C-dots

UV-Vis spectra obtained over a scan range of 200 – 900 nm for the blue, green and yellow luminescence C-dots are shown in Fig 6a-c. The absorption maxima fall in the region (190-390) with a tail extending to the visible region [36] were relatively broader for both the green and yellow luminescence colour (Fig. 6b-c), but narrower for the blue C-dots (Fig. 6a). The two patterns may be attributed to non-uniform size distribution in the former while the latter sizes were relatively more uniform. In the representative example, observed maxima were at 233nm, 239nm and 242nm for blue, green and yellow C-dot respectively which were ascribed to the $\pi \rightarrow \pi^*$ transitions of C=C present on C-dots, while the seeming shoulder at 296nm and 302nm for green and yellow (Fig. 6b-c) were due to $n \rightarrow \pi^*$ of carbonyl groups (C=O) [37]. The observed blue shift in the absorption maxima is indicative of a strong confinement with decrease in size [38].

3.6 Band Gap Determination

The band gap energy values of the prepared C-dots were calculated from experimentally obtained UV-Vis absorption spectra cut-off edges [39-40]. The UV-Vis spectra obtained for blue, green and yellow luminescence C-dots (Fig. 6a-c) have strong cutoff wavelengths (λ) at 311×10^{-9} m, 347×10^{-9} m and 467×10^{-9} m respectively. The values of the band gap energies (Table 2) obtained using Equation 1 indicates that the C-dots are in the semiconductor range. The blue-luminescence C-dot has relatively higher band gap energy which suggests a much wider energy separation compared to the green and yellow C-dots respectively. This energy separation increases as the size decreases for semiconductor a nanocrystal which is complemented by the shift to the blue end.

Table 1: Reaction conditions for tunable C-dots

S/N	Source of starch	Acid	Reaction time (min)	Luminescence color under UV light 365 nm
1	Cassava	2M H ₂ SO ₄	3-5	Blue
2	Potato	2M H ₂ SO ₄	3-5	Blue
3	Rice	2M H ₂ SO ₄	3-5	Blue
4	Yam	2M H ₂ SO ₄	3-5	Blue

5	Cassava	Conc. H ₃ PO ₄	3-7	Blue
6	Potato	Conc. H ₃ PO ₄	3-7	Blue
7	Rice	Conc. H ₃ PO ₄	3-7	Blue
8	Cassava	2M H ₂ SO ₄	5-10	Green
9	Potato	2M H ₂ SO ₄	5-10	Green
10	Rice	2M H ₂ SO ₄	5-10	Green
11	Cassava	Conc. H ₃ PO ₄	30-60	Yellow
12	Potato	Conc. H ₃ PO ₄	30-60	Yellow
13	Rice	Conc. H ₃ PO ₄	30-60	Yellow
14	Yam	Conc. H ₃ PO ₄	30-60	Yellow

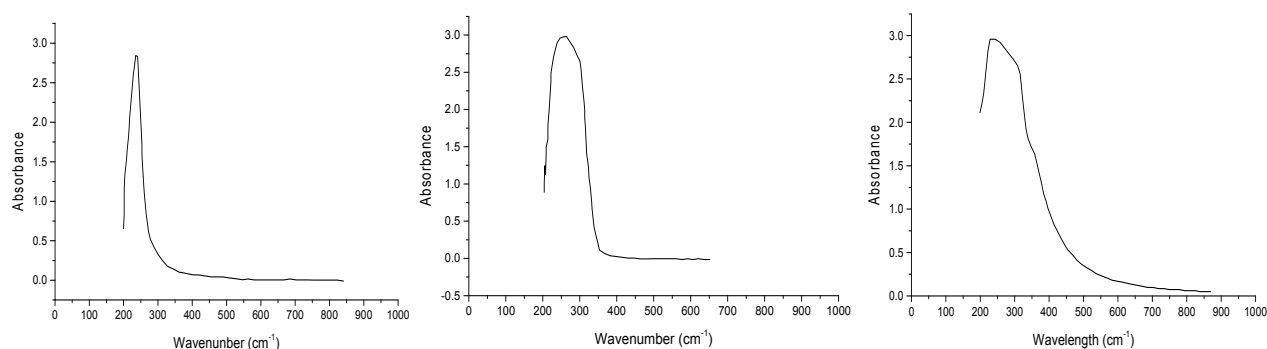


Fig. 6(a): Blue luminescence C-dots Fig 6(b): Green luminescence C-dots Fig. 6(c): Yellow luminescence C-dot

Table 2: Calculated Band Gap Energy (E) for the synthesized luminescence C-dots.

Fluorescence C-dots	Wavelength(nm)	Band Gap Energy (eV)
Blue	311	3.99
Green	347	3.58
Yellow	467	2.66

Where $1\text{eV} = 1.6 \times 10^{-19}$ Joules (conversion factor)

4. Conclusion

Tunable luminescence C-dots have been prepared via a facile one-step acidic mediated microwave assisted carbonization of starch precursors (used as carbon source). The approach adopted is simple and cost effective. The result obtained from FTIR studies revealed diagnostic bands for (OH), (C=O), (C-O), and (C=C) that characterize the C-dots. Optical studies show that the luminescence behavior of the C-dots (blue, green or yellow) strongly depends on the reaction conditions. Particularly, the yellow C-dots were obtained only with phosphoric acid passivation at lower reaction temperature after neutralization with base. The band gaps of the C-dots were calculated using cutoff values from UV-Vis and found to fall within the semiconductor range. Finally, the synthesized C-dots exhibited

strong luminescence and good solubility which makes them potential materials for probes in biological applications.

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LIST OF SYMBOLS

BDH	
CQD	Carbon Quantum Dots
C-dots	Carbon Dots
FTIR	Fourier Transform Infrared
UV	Ultra violet
UV-Vis	Ultraviolet Visible Spectroscopy

