Facile preparation of high fluorescent carbon quantum dots from orange waste peels for nonlinear optical applications

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Abstract
A facile and eco-friendly hydrothermal method was used to prepare carbon quantum dots (CQDs) using orange waste peels. The synthesized CQDs were well dispersed and the average diameter was 2.9 ± 0.5 nm. Functional group identification of the CQDs was confirmed by Fourier transform infrared spectrum analysis. Fluorescence properties of the synthesized CQDs exhibited blue emission. The fluorescence quantum yield of the CQDs was around 11.37% at an excitation wavelength of 330 nm. The higher order nonlinear optical properties were examined using a Z-scan technique and a continuous wave laser that was operated at a wavelength of 532 nm. Results demonstrated that the synthesis of CQDs can be considered as promising for optical switching devices, bio-scanning, and bio-imaging for optoelectronic applications.

KEYWORDS
CQDs, fluorescence quantum yield, HR-TEM, hydrothermal method, Z-scan analysis

1 | INTRODUCTION

Carbon dots are new promising carbonaceous materials that have attracted considerable attention in numerous research areas due to their unique physical properties.[1-4] In the ever-expanding field of nanomaterial research, researchers are exploring new carbon source materials from natural sources that are simple, of low cost with high performance, and with the possibility of green synthesis a highly desirable factor.[5-10] Recently, reports have detailed that organic molecules with an extended delocalized π-electron system possess perfect nonlinear optical values.[11] Among various nonlinear optical materials, ‘green’ carbon source CDs have shown the maximum nonlinear optical properties. Recent articles have demonstrated CQD synthesis using many natural materials and with an option to re-use natural waste.[12-21] Orange waste peels are underused natural resources and it is still challenging to use these leftover residues effectively. For CQD synthesis, carbonization of glucose, sucrose, glycol, glycerin, and citric acid has received significant attention.[22]

Some previous reports have described the preparation and application of orange peel carbon dots as fluorescence markers, as bio-imaging agents, in photoluminescence, as efficient catalysts, and in energy sciences.[23-25] However, detailed reports for the nonlinear optical performance of CQDs is still absent and this article attempts to fill this gap. To the best of our knowledge, this article describes the first attempt to study third harmonic generation properties of CQDs prepared from orange peels.

In this present work, we succeeded in CQD synthesis using orange waste peels as a carbon source via a hydrothermal method. The synthesized CQDs were characterized using high-resolution transmission electron microscopy, Fourier transform infrared spectroscopy (FT-IR), and powder X-ray diffraction (PXRD) analysis. The linear optical properties of the CQDs were examined over the ultraviolet (UV)–visible
spectrum and fluorescence with high quantum yield. Third-order non-linear optical parameters of CQDs were investigated using a Z-scan technique and a continuous wave laser operated at a wavelength of 532 nm. These synthesized orange waste peel CQDs would be a suitable material for all optical limiting, optical switching, and fluorescence imaging applications.

2 | EXPERIMENTAL

2.1 | Materials and methods

Orange waste peels were collected from a local fruit market in Karaikudi, Tamil Nadu, India. The fresh orange waste peels were cut into small pieces and washed with double-distilled water. The waste peels were kept in daylight for 6 days and then carbonized at 60°C under an open atmosphere. Citric acid and ammonia were purchased from Merck (AR) grade and used without any further purification.

2.2 | Preparation of orange waste peel CQDs

Synthesis of carbon quantum dots (CQDs) is illustrated in Figure 1. Initially, 2 g orange waste peel (yielded carbon) and 2 g citric acid were mixed homogeneously with 30 ml of double-distilled water and then 5 ml of ammonia was added to the solution to pH 7. The dispersed solution was transferred to a Teflon-lined stainless steel autoclave and heated at 200°C for 6 h. After 6 h, the autoclave was allowed to cool naturally at room temperature. The reaction solution was ultrasonicated for 50 min and centrifuged at 5000 rpm for 1 h under ambient conditions. The precipitate and supernatant were collected separately for further characterization.

2.3 | Instrumentation techniques

The synthesized carbon dots were subjected to the Bruker AXS D8 Advance X-ray powder diffractometer system with CuKα radiation (1.5404 Å) at a scan speed of 0.1 min^{-1} and with 2θ range between 10–80°. The HR-TEM images were measured using a Joel/JEM2100 microscope with an accelerating voltage of 200 kV. FT-IR spectra were recorded at room temperature on a Perkin Elmer (Spectrum two) spectrometer, range 400–4000 cm^{-1}. UV absorption spectra were recorded using a Perkin Elmer UV–visible spectrometer (Lambda 35) in the wavelength range 200–800 nm. Fluorescence measurements were recorded using a spectrofluorimeter (Jobin yvon, Fluorolog-3-11) equipped with a xenon lamp (450 W) that acted as an excitation source. Third-order nonlinear optical properties of the CQDs were investigated using a continuous wave laser (100 mW) operated at a wavelength of 532 nm.

3 | RESULTS AND DISCUSSION

3.1 | High-resolution transmission electron microscopy (HR-TEM)

The morphology of the as-prepared CQDs was confirmed using HR-TEM. Figure 2(a) shows the well dispersed and uniform CQDs. Figure 2(b) shows that the lattice spacing of 0.25 nm was lower than the lattice plane of graphite materials (0.34 nm).[18] Particle size
distribution of the CQDs is shown in Figure 2(c) and was calculated by measuring several particles, giving a mean diameter of 2.9 ± 0.5 nm. Small nanoparticles were not observed in the CQDs due to particle agglomeration such that only large particles were observed; this issue could influence the optical properties of the CQDs.[26] The PXRD pattern of the as-prepared CQDs is shown in Figure 2(d), and displayed a broad diffraction peak centred at 2θ = 22–24° that was attributed to the carbon structure.[27] HR-TEM and PXRD results confirmed the presence of CQDs.

### 3.2 Functional group identification: FT-IR

FT-IR spectroscopy is an analytical technique used here to identify the surface functional groups of the CQDs. Figure 3 shows the FT-IR spectrum of the prepared CQDs and identified carboxylic functional groups on the CQD surface. The absorption peaks positioned at 3437 and 660 cm⁻¹ could be attributed to the stretching vibration of –OH groups, related to the O–H bonds on the carbon surface and also adsorbed water on the product surface.[28–33] Peaks at 1637 and 1406 cm⁻¹ were due to the stretching vibration of the carboxylic group. These results indicated that there were large numbers of residues indicated as hydroxyl and carboxyl groups on the CQD surface.

### 3.3 UV–visible spectral analysis

Figure 4 shows the absorption spectrum of the CQDs. In the spectrum, lower cutoff wavelengths for the CQDs were observed at 235 and 332 nm. Absorption of the CQDs was attributed to the π–π* transition of aromatic C=C bonds and the n–π* transition of surface

**FIGURE 2** (a) High-resolution transmission electron microscopy image, (b) lattice spacing, (c) particle size distribution, and (d) powder X-ray diffraction pattern of carbon quantum dots

**FIGURE 3** Fourier transform infrared spectrum of carbon quantum dots

**FIGURE 4** Ultraviolet–visible light absorption spectrum of carbon quantum dots
functional groups such as C=O. A broad peak at 332 nm in the visible absorption spectrum of the CQDs appeared due to trapping of large amounts of excitation energy, leading to huge amounts of emission at 365 nm excitation and indicated that the prepared CQDs were fluorescent. The inset in Figure 4 shows CQDs under visible light and UV light at 365 nm. The linear optical absorption (LOA) coefficient ($\alpha$) was calculated using eqn (1):

$$\alpha = \frac{2.303 \times \Delta A}{d}$$  

(1)

where ‘$\Delta A$’ is the absorption and ‘d’ is the thickness of the cuvette. The extinction co-efficient (K) gives the amount of absorption of the CQDs and was calculated using eqn (2):

$$K = \frac{\alpha \lambda}{4\pi}$$  

(2)

where $\lambda$ is the wavelength. A graph was drawn of extinction coefficient and wavelength (Figure 5). The linear refractive index ($n_0$) of the prepared CQDs was calculated using eqn (3):

$$n_0 = -(R + 1) \pm \sqrt{R + 1}$$  

(3)

where $R$ is the reflectance of the sample. The calculated linear refractive index ($n_0$) of the CQDs is shown in Figure 5.

### 3.5 Quantum yield measurements

Fluorescence quantum yields (QY) of the synthesized orange waste peel CQDs were measured according to an established procedure. Quinine sulphate was taken as the standard reference. The prepared CQDs were diluted to four different concentrations in distilled water for absorbance measurement. QY was calculated using the following eqn (4):

$$QY_s = QY_R \times \frac{n_{s}^2}{n_{R}^2} \times \frac{I_s}{I_R} \times \frac{A_s}{A_R}$$  

(4)
where QY_S and QY_R are the QYs of CQDs and the reference, $n_s^2$ and $n_R^2$ are the refractive indices of the solvents, I_S and I_R are the fluorescence measured integrated emission intensities of prepared CQDs and reference, and $A_s$ and $A_R$ are the absorption excited wavelengths. The QY of the orange waste peel CQDs was 11.37% at excitation wavelength 330 nm. This was due to the presence of carboxylic groups, which play a key role in the generation of CDs with high quantum yield.\[16\] Synthesized CQDs were compared with various natural precursors for fluorescence colour, size, quantum yield, and various applications, summarized in Supporting Information Table S1.

### 3.6 Open and closed aperture Z-scan analysis

Sheik-Bahae et al.\[48\] proposed a Z-scan technique for accurate determination of both nonlinear refractive (NLR) index and the nonlinear absorption (NLA) co-efficient of nonlinear optical materials (NLP). Figure 8 shows a scheme of the Z-scan technique in which a continuous wave laser (100 mW) at an excitation wavelength of 532 nm, with a focal length of lens 103 mm was used. The prepared orange waste peel CQDs were dispersed using ethylene glycol. To avoid any cumulative and thermal effects, the material was ultrasonicated before and after each measurement. The diluted solutions were put in a 1 mm cuvette with transmittance of ~65%, mounted on a translation stage that shifted across the focal length from negative (−z) to positive (+z) axes by directing the laser beam.

In closed aperture (CA) mode transmission, a laser beam was passed through the prepared material via the far-field aperture and the O/P intensity (aperture radius 1.25 mm) was collected using a digital power meter. If the sample phase shift has a positive nonlinearity (self-focusing $n_2 > 0$ occurs), the transmission peak will trail the valley and if the phase shift is negative (self-defocusing $n_2 < 0$ occurs), the valley will trail the peak. As shown in Figure 9, the CA Z-scan curve of the CQD materials exhibited (self-defocusing) negative nonlinearity.

Open aperture (OA) mode was employed by measuring the laser transmission in the nonappearance of the aperture. In this mode, the maximum lies near the focus ($z = 0$) if the intensity transmission peak is high and indicates saturation absorption (SA) or, conversely, if the intensity of the transmission is less (valley) this indicates reverse saturation absorption (RSA). Figure 10 shows the OA Z-scan curve of the material, which exhibited RSA. The difference between the normalized transmission peak and the valley ($\Delta T_{p-v}$) in the normalized Z-scan curve can be written in terms of axis phase shift at the focus, given below (eqn 5):

$$|\Delta \phi| = \frac{\Delta T_{p-v}}{0.406 (1-s)^{\frac{1}{2}} \lambda^2}$$

where ‘s’ is the aperture linear transmission ($s = 1 - \exp(-2r_a^2/\omega_a^2)$), ‘r_a’ is the aperture hole radius, and ‘$\omega_a$’ is the laser spot radius of the screen. From CA Z-scan analysis, the NLR index ($n_2$) of the synthesized CQDs was calculated using the relationship (eqn 6):

$$n_2 = \frac{\Delta \phi \lambda}{2 \pi I_0 L_{eff}} (m^2/W)$$

The NLA co-efficient ($\beta$) was estimated (eqn 7),

$$\beta = \frac{2\sqrt{2} \Delta T}{\lambda I_{eff}} (m/W)$$
TABLE 1  Nonlinear optical parameters of the as-synthesized carbon quantum dots

<table>
<thead>
<tr>
<th>Third-order nonlinear optical parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser beam wavelength (λ)</td>
<td>532 nm</td>
</tr>
<tr>
<td>Lens focal length (f)</td>
<td>103 mm</td>
</tr>
<tr>
<td>Optical path length</td>
<td>675 mm</td>
</tr>
<tr>
<td>Beam radius (ω₀)</td>
<td>3.5 mm</td>
</tr>
<tr>
<td>Radius of aperture (r₀)</td>
<td>1.25 mm</td>
</tr>
<tr>
<td>Sample thickness (L)</td>
<td>1 mm</td>
</tr>
<tr>
<td>Nonlinear absorption co-efficient (β)</td>
<td>2.1509 × 10⁻⁴ cm²/ w</td>
</tr>
<tr>
<td>Nonlinear refractive index (n₂)</td>
<td>7.1690 × 10⁻⁹ cm²/ w</td>
</tr>
<tr>
<td>Real part of the third-order susceptibility</td>
<td>2.7520 × 10⁻⁷ esu</td>
</tr>
<tr>
<td>Imaginary part of the third-order susceptibility</td>
<td>3.5013 × 10⁻⁸ esu</td>
</tr>
<tr>
<td>Third-order nonlinear optical susceptibility</td>
<td>2.7742 × 10⁻⁷ esu</td>
</tr>
</tbody>
</table>

where ΔT is the normalized transmission valley of the OA Z-scan curve. Calculated values for NLR index (n₂) and NLA (β) were used to determine the [Re(χ(³))] and [Im(χ(³))] parts of the third-order nonlinear optical susceptibility (χ(³)) that can be easily estimated using the following relationship (eqn 8) [49,50]:

\[
\text{Re}(\chi^{(3)}) (\text{esu}) = \frac{10^{-4} \varepsilon_0 c^2 n_0^2 n_2}{\pi} \quad (\text{cm}^2/\text{w})
\]

\[
\text{Im}(\chi^{(3)}) (\text{esu}) = \frac{10^{-2} \varepsilon_0 c^2 n_0^2 \omega^2}{4\pi^2} \quad (\text{cm}/\text{w})
\]

Here, 'ε₀' is the electric permittivity and 'c' is the speed of light. The third-order nonlinear optical susceptibility value of the synthesized CQDs was obtained using eqn (9):

\[
\chi^{(3)} = \sqrt{(\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2}
\]

The estimated third-order NLR index (n₂), NLA co-efficient (β), and third-order nonlinear susceptibility (χ(³)) values are listed in Table 1. The synthesized CQDs would be acceptable for all optical switching applications if the following conditions single photon (W > 1) and multiphoton (T < 1) were satisfied. The values for qualified T and W were estimated using the following relationship (eqn 10) [51]:

\[
W = \frac{n_2 l_0}{\alpha}
\]

\[
T = \frac{\beta \lambda}{n_2}
\]

where n₂ is the NLR index, l₀ is the intensity of the laser beam at the focus, α is the absorption co-efficient, and β is the NLA co-efficient. Calculated values were T = 0.0159 and W = 6.993, which were reasonably good. Therefore these CQDs were highly promising materials for use in optical switching devices.

4 | CONCLUSION

This facile, green synthesis approach worked well based on morphology, particle size, and significant area of the prepared carbonaceous material. FT-IR spectrum analysis indicated that orange peels were successfully converted to CQDs. From the fluorescence spectrum, it was clear that the particles responded to visible light with a QY of 11.37%, and could be used in fluorescence imaging. The encouraging results of the Z-scan analysis suggested that the CQDs were a promising material for photonic devices applications.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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REFERENCES

SUPPORTING INFORMATION

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