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论文题目： Household Synthesis of Carbon
Quantum Dots from Table Sugar: A Study of
Methodology, Properties, and Density
Functional Theory Calculations

Household Synthesis of Carbon Quantum Dots from Table Sugar: A Study of Methodology, Properties, and Density Functional Theory Calculations

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Abstract

Carbon quantum dots (CQDs) are nano-carbon structures with luminescence properties. They are widely applied across disciplines, including chemical sensing and bioimaging. However, they can often be complicated and toxic to synthesize, and their structures are not precisely known. This paper aims to put forward a feasible, simple and environmental-friendly method for CQDs synthesis, and shed some light on the structures and properties of CQDs from a theoretical perspective. The paper begins by presenting and detailing a simple methodology that allows for the synthesis of CQDs in a household kitchen using table sugar with the top-down approach. Building on the CQDs synthesized using that approach, the paper then examines their properties and molecular structures by performing Fourier-transform infrared (FTIR) spectroscopy and Ultraviolet–visible (UV-Vis) absorption spectroscopy. Finally, using density functional theory (DFT) computations, this paper proposes an optimized geometry of the synthesized CQDs, and their corresponding molecular orbitals, electron density, among other theoretical properties.

Keywords:

Carbon Quantum Dots, Density Functional Theory, Top-down Synthesis, Nano-carbon

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1. Introduction

Quantum dots are fluorescent nano semiconductor particles usually smaller than 10nm. [1] Due to their unique fluorescence properties, they are widely applied as markers, sensors, photodetectors, and even used in displays. [1, 2] However, the main-structure of many quantum dots can contain heavy metal, causing significant toxicity to human and the environment. [3] Carbon Quantum Dots (CQDs) are emerging as a more and more important class of quantum dots because of their environmental friendliness. They are composed of nano-carbon structures, and have the fluorescence characteristics of quantum dots, but don't contain heavy metal elements, making them nontoxic with high biocompatibility. [4] CQDs are applied in various fields such as bioimaging, medical diagnosis, biosensing, chemical sensing, photocatalysis, and photovoltaic devices. [5] Current methods for CQD preparation can be classified into bottom-up approaches (polymerization of smaller particles), and top-down approaches (breaking down of macromolecules). Common methods include Arc Discharge, Laser Ablation, Acidic Oxidation, Electrochemical Oxidation, and microwave-assisted synthesis. [6] However, many of these current methods have complicated setups, utilizing acids and other materials which may harm humans and the environment. [7] Compared with them, the synthesis in this study is a feasible, simple and environmental-friendly method to apply, where it can even be conducted at home. Moreover, since the structures of CQDs are not precisely known [8], a molecular model for the prepared CQDs is proposed based on density functional theory (DFT) to further elucidate the structures of CQDs. With these results, the study is aimed to contribute to the development for the convenient synthesis of CQDs as well as the investigation of the structure and properties of CQDs.

2. Methodology

2.1. Preparation of CQDs

Carbon Quantum Dots were prepared using a top-down approach by breaking down larger carbon compounds (saccharides) into smaller nano-dots. In a typical synthesis, 80.00g of table sugar is thoroughly dissolved in 240mL of distilled water. 60mL of vinegar is then added into the sugar solution and the mixture is microwaved by using a microwave oven at medium heat (525W) for 5 minutes. The resulted mixture is an acidic solution of glucose and fructose. By neutralizing it with 20.0 grams of baking soda, a basic solution with a final pH of 7.62 is obtained. After heating the solution for 5 minutes in two intervals using a microwave oven under medium heat (525W), the CQD solution is synthesized.

2.2. Experimental Characterization

The luminescence properties of the carbon quantum dots are examined by a 395nm UV flashlight to confirm the formation of CQDs. The functional groups and bonds present in the molecular structure of the CQD is characterized by Fourier-transform infrared (FTIR) spectroscopy (PerkinElmer Spectrum Two FT-IR Spectrometer). The transitions from the functional groups composing the surface states of CQD, as well as the band gap of the molecule is evaluated by Ultraviolet-visible (UV-Vis) absorption spectroscopy (PerkinElmer Lambda 365 UV/VIS).

2.3. DFT Modeling and Calculation

To further investigate the molecular structure and other properties of the synthesized CQDs, the GaussView6 software is used to construct a model based on the performed FTIR spectra and the functional groups it indicates. After constructing the model, optimization and frequency calculations are performed on the Gaussian 09 platform with the 6-31+g(d) basis set using Ground State DFT

B3LYP. The optimized geometry, dipole moments, electron density, as well as HOMO/LUMO orbitals were investigated based on the calculation.

3. Results and Discussion

3.1 Success of Synthesis and Luminescence Properties



Fig 1, The Materials used for CQD synthesis: Table Sugar/sucrose (Left); White vinegar (Middle); Baking soda/sodium bicarbonate (Right).

This paper's synthesis process is simple, green, and can be easily performed in a household kitchen. The synthesis process uses a top-down approach, breaking down larger carbon compounds (saccharides) into smaller nano-dots. Unlike other time consuming, difficult, and potentially hazardous approaches to Carbon Quantum Dots synthesis, the method in this research can be carried out using household equipments and materials. The experimental methods for a typical synthesis is described in 2.1, and a diagram of the raw materials and the process is shown in figure 1. Moreover, the process uses minimal energy and contains no toxic/caustic chemicals, making it a great method for synthesis. During synthesis, sucrose is broken down into glucose and fructose through the inversion process. The monosaccharides in a basic solution then starts to nucleate and grow CQDs. [7] Additional energy is applied to the system through a microwave oven to initiate and speed up the formation process. As CQDs form in the solution and the concentration increases, the color of the solution darkens (Figure 2). [14]

To confirm the success of the synthesis in a visual and preliminary way, the synthesized concentrated CQD solution is diluted in water, and a 395nm UV flashlight is used to excite the CQDs. The resulting carbon quantum dots exhibit a green fluorescence as shown in Figure 3.

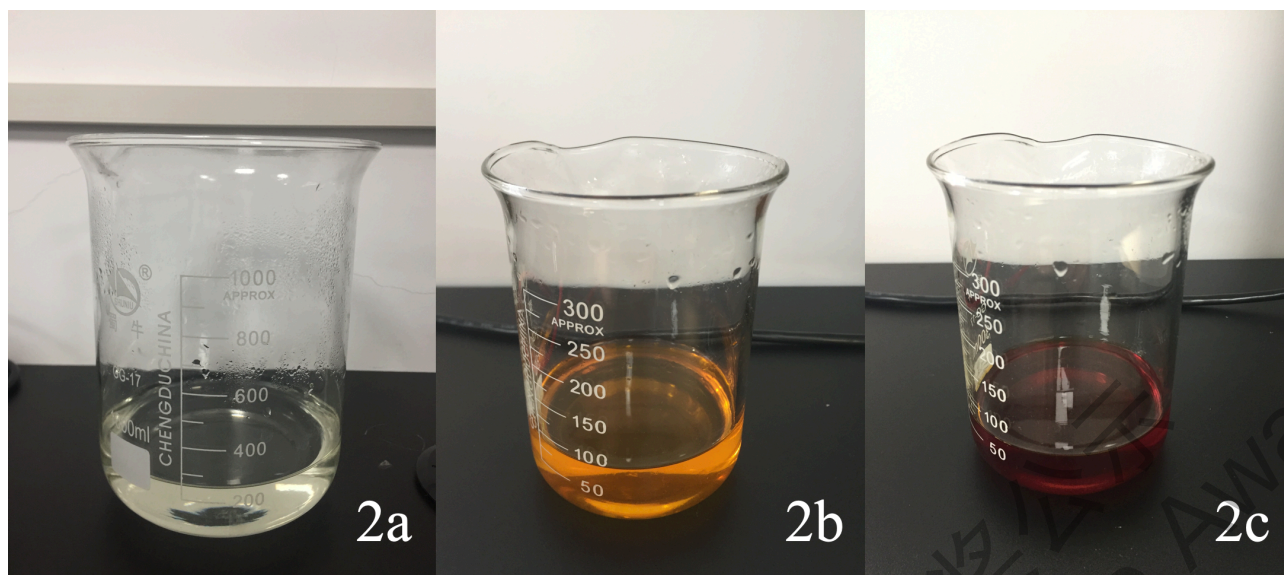


Fig 2, The Formation of CQDs: Solution before microwaving (a); Solution after 2.5min microwaving (b); Solution after 5min microwaving (c).



Fig 3, Luminescence Properties of CQDs : Diluted CQD solution under normal daylight (Top Left); Diluted CQD solution exhibiting green fluorescence under UV flashlight (Top Right and Bottom);

3.2. Experimental Characterization and Elucidation of CQD structure

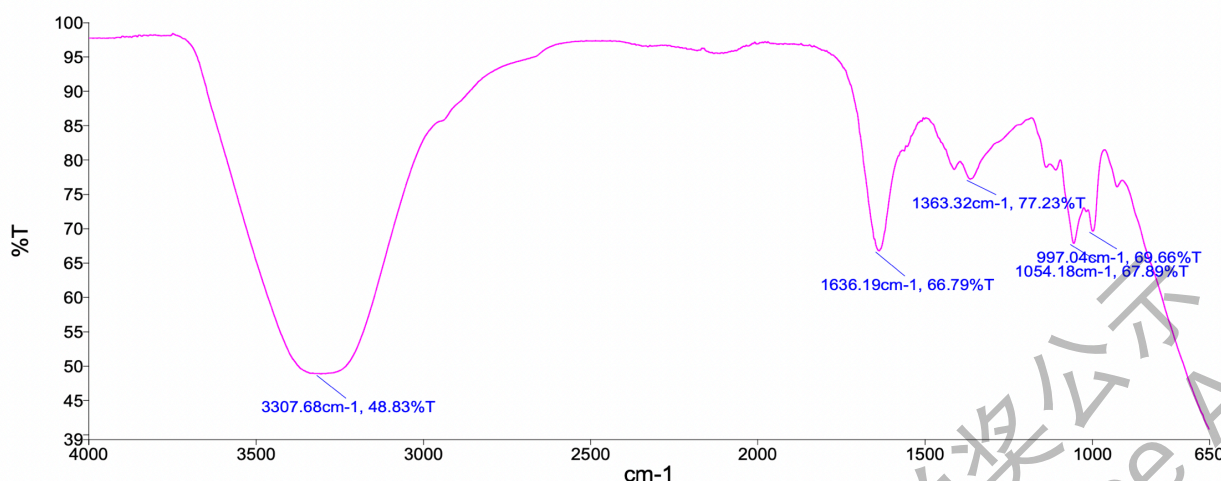


Fig 4, The experimental FTIR spectrum for synthesized Carbon Quantum Dots.

The structure of CQDs are characterized to be single layered graphene terminated with oxygen-containing functional groups. [9] To further investigate the properties of the CQDs synthesized from this method and its molecular structures, FTIR and UV-Vis spectroscopy is performed.

FTIR helps determine the functional groups on the surface of CQDs. Figure 4 shows the FTIR spectrum of the CQD sample. The strong absorption peak at 1639 cm^{-1} indicates the presence of C=C stretching and C=O stretching. [10] The C=C stretching vibration mode indicates the presence of CQDs, whose main structure is single-layered graphene. The C=O stretching indicate the presence of -C=O groups in the CQD structure. A strong and very broad absorption peak at 3307 cm^{-1} demonstrates the -OH stretching mode, indicating the presence of -OH functional groups as well as the formation of hydrogen bonds with the solvent. [11, 12] The peak at 1363 cm^{-1} indicates the C-H bending vibrational mode, signifying possible methyl and -CH₂ functional groups as well as the termination of the CQD with hydrogen. [12, 14] The peak at 1054 cm^{-1} clearly illustrates C-O stretching found in carboxyl functional groups. [7, 12] Lastly, a small peak at 997 cm^{-1} signals the C=C bending mode. To summarize, the FTIR results demonstrate the successful synthesis of CQD structures, and show that the terminal functional groups of the CQD include carboxyl, methyl, -CH₂, -OH, and -C=O. The terminal structure is also possibly saturated with C-H bonds. The overall spectrum is similar to the results reached by Zaman et. al., and Ma et. al. in their synthesis using other methods, again confirming the success of the synthesis method presented in this study. [12, 13]

Figure 5 shows the UV-Vis spectrum for the CQD sample. The peak at around 206 nm signifies the π - π^* transition [15], while the peak at 284 nm represents the n - π^* transition [16]. The strong absorption peak at 206 nm is very similar to the results achieved by Chae et. al. [17] in a bottom-up synthesis approach. The peak at 284 nm is likely indicating the C-O transitions in the CQD, signifying oxygenic functional groups like -C=O and -COOH. [10]

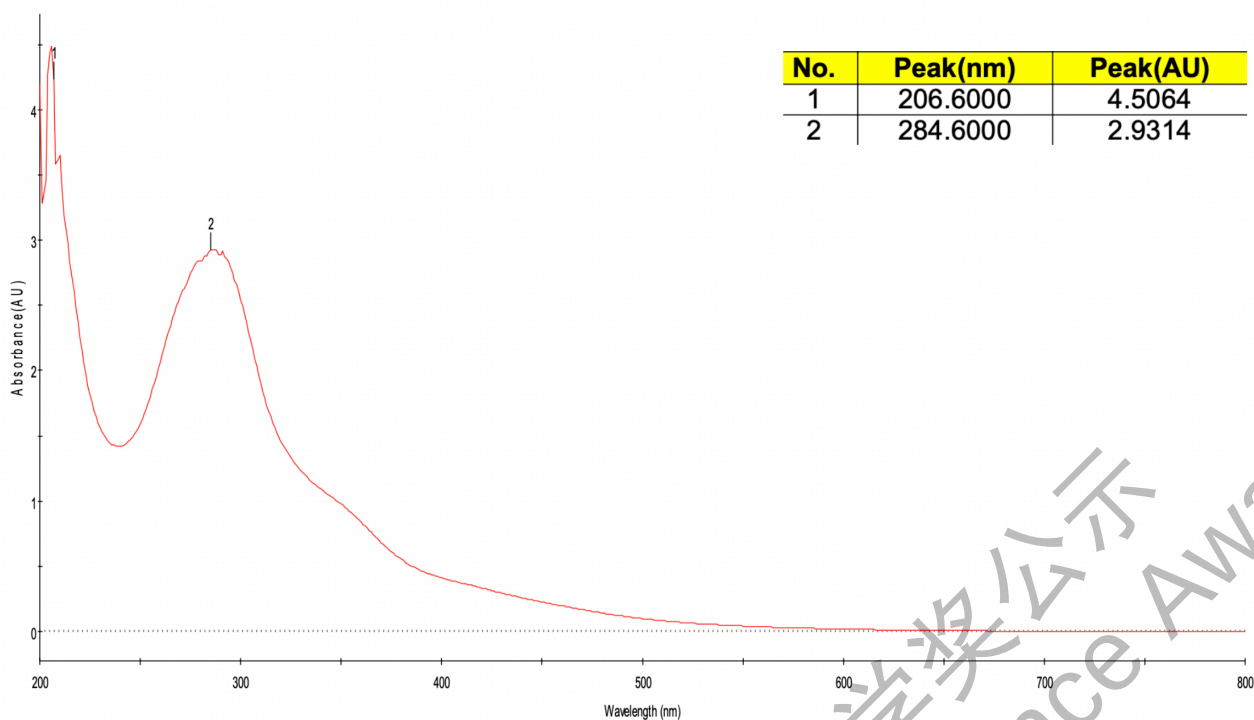


Fig 5, The experimental UV-Vis spectrum for synthesized Carbon Quantum Dots.

3.3. Experimental Molecular Band Gap

The molecular band gap is a crucial characteristic for fluorescent nano-particles, as it illustrates the energy between the conduction and valence bands. The experimental band gap for synthesized CQDs is calculated from the UV-Vis absorption data. From the Beer-Lambert Law, the expression of the absorption coefficient α can be found in terms of the absorbance in the UV-Vis data. [18] The energy for each excitation wavelength can also be found by using the Planck relation ($E=hc/\lambda$).

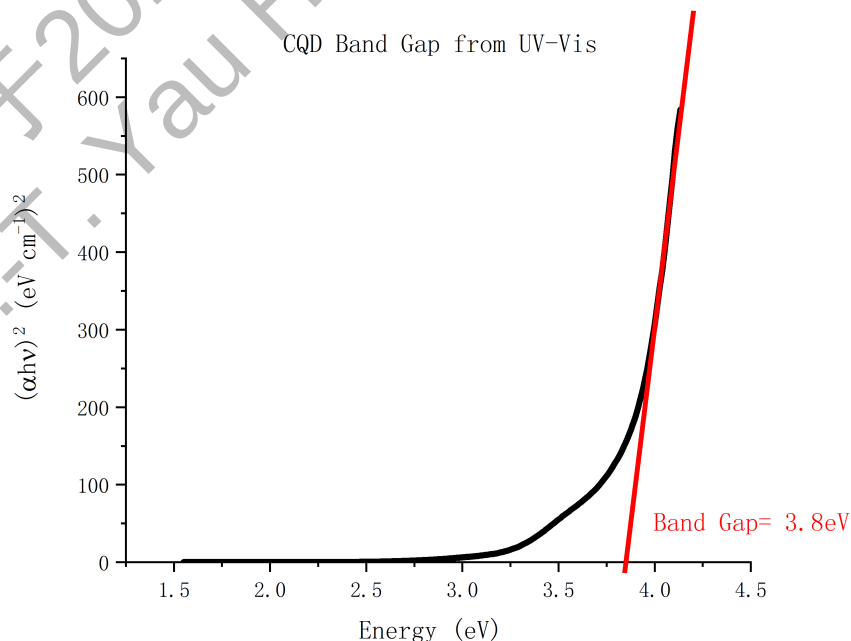


Fig 6, The experimental Tauc plot and band gap for CQDs.

Finally, $(\alpha h\nu)^\gamma$, with $\gamma=2$ for direct allowed transitions as in the CQD [19], is plotted against the calculated energies in a Tauc plot (Figure 6). It can be seen that the graph approaches a linear relationship as the energy increases. This linear trend line is approximated, and the x-intercept gives the experimental band gap according to the Tauc relation $(\alpha h\nu)^\gamma=A(h\nu-E_g)$ [18, 19], which is calculated to be around 3.8 eV for the CQD sample.

3.4. Gaussian Molecular Modeling

It is known that CQDs are single layered graphene structures with edge functional groups [9]. The modeling of the basic structure, including the sizes, took inspiration from the work by Ambrusi et. al. [20] Using the characterization results from the FTIR, as described in 3.2, the edge functional groups for the CQDs are determined. With these functional groups and the central graphene structure, a model for the molecular structure of our CQDs is successfully proposed and constructed in GaussView6.

3.5. Molecular Geometry Optimization with DFT calculation

After constructing the molecular structure model, a DFT optimization calculation of the structure is performed using the 6-31+g(d) basis set and DFT Ground State B3LYP methods, giving an optimized molecular geometry (Figure 7a). The final optimized total energy was calculated to be -915.63 Hartree. The calculation presents the optimized bond lengths and bond angles, visualized in figure 7a. Figure 7b shows the visualized calculated charge distribution and dipole moment of the CQD molecule model resulting from the DFT optimization calculation. The darker green-colored atoms have greater positive charge, while the darker red-colored atoms have greater negative charge.

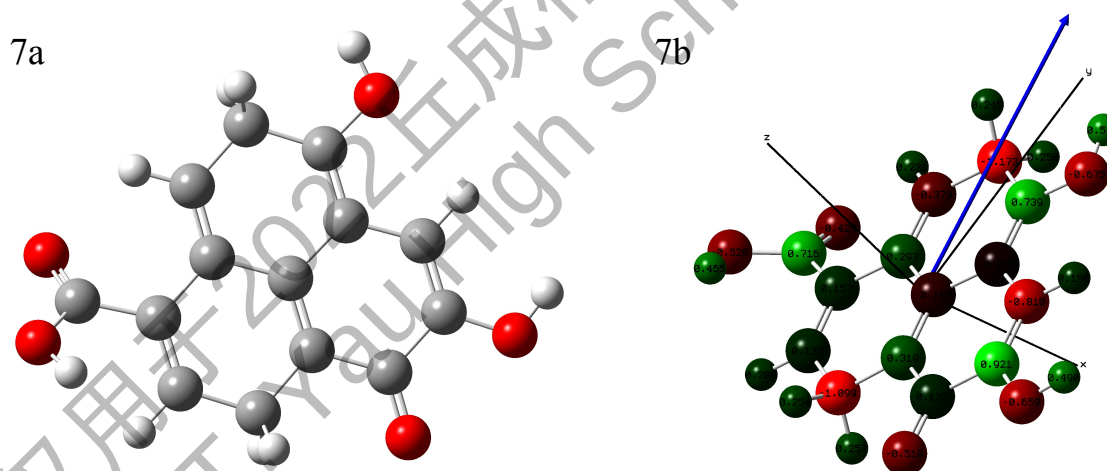


Fig 7, Optimization visualization of calculated DFT results: The final optimized geometry at -915.63 Hartree (a); The dipole moment vector and charge distribution (labelled by colors) of the optimized structure (b).

3.6. Confirmation of Modeling with Theoretical IR spectrum

To verify the accuracy of the model for the synthesized CQD, the optimized geometry of the molecule is used as a new input file for calculating the vibration frequencies of the molecule. The calculation is performed through the same method and basis set. Figure 8 illustrates the IR spectra for the CQDs. Figure 8a illustrates the IR peaks spectrum before performing the Fourier transform, while figure 8b shows the experimental FTIR spectrum for comparison. The computed theoretical

spectrum shows many similar peaks to the experimental one. Firstly, the peaks near 1600 and 1800 are the C=C double bond stretching mode and C=O stretching mode, clearly corresponding to the combined peak at 1639 cm^{-1} in the experimental result. The peaks near 1350 cm^{-1} from C-H bending mode vibrations matches the 1360 cm^{-1} experimental peak very well as well. Finally, the C-O stretching peak at around 1050 cm^{-1} is also clearly simulated. The -OH stretching peaks at around 3000 cm^{-1} and 3700 cm^{-1} match with the experimental one for the general frequency region. However, they do not match up well with the very broad peak seen in the experimental results. This is caused because the computations only calculate a single molecule, while the experiment is performed on multiple molecules, resulting in broader peaks for experimental results. This may also be due to the poor performance of B3LYP for calculating long-range interactions, and possibly the lack of simulations regarding the hydrogen bonds with the solution. Overall, the theoretical model correctly models the CQD synthesized from the process, including the major functional groups.

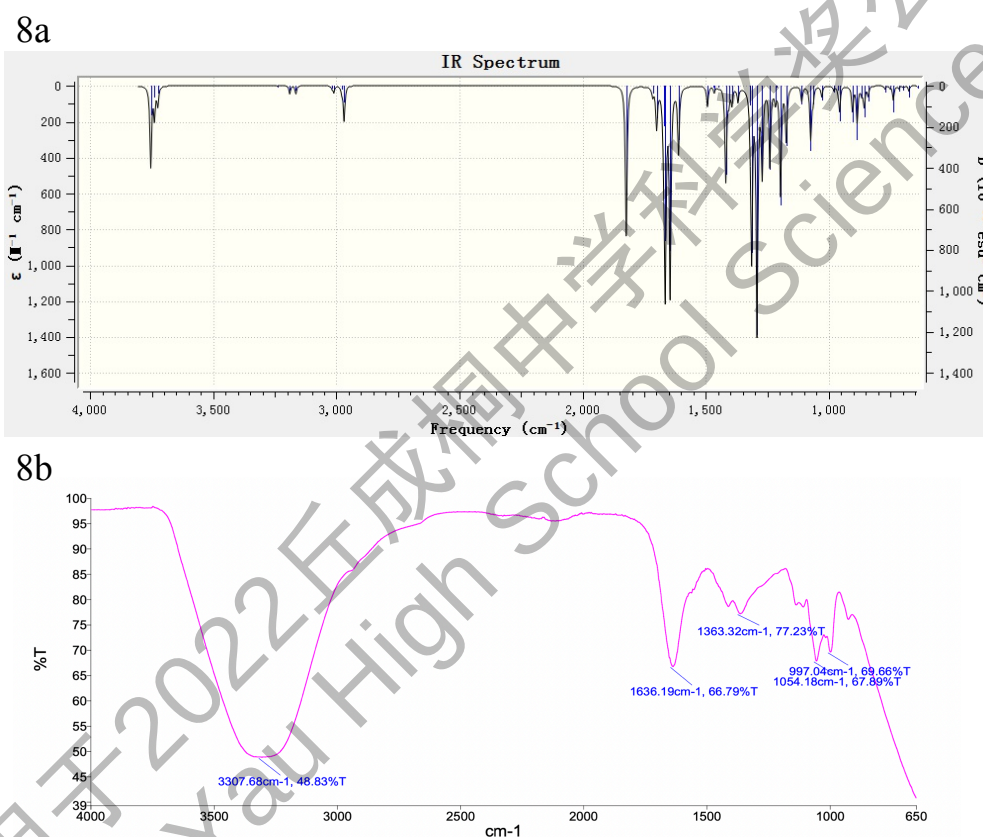


Fig 8. The DFT-calculated IR spectrum and the experimental FTIR spectrum for comparison of synthesized Carbon Quantum Dots.

3.7. DFT findings: Molecular Orbitals and Electron Density

To further investigate more properties with the CQD, the calculated molecular orbitals and electron density of the molecule is studied. A total of 376 orbitals were found for the molecule, of which orbital 68 is the LUMO (lowest unoccupied molecular orbital) and orbital 67 is the HOMO (highest occupied molecular orbital), with energies of -0.22212 hartree and -0.09219 hartree respectively (Figure 9a). The HOMO-LUMO band gap for the theoretical calculation of the proposed model can be calculated to be 0.12993 Hartree, or 3.5356 eV. This result is quite similar to the experimental results of the band gap, 3.8 eV, as described in 3.3. The LUMO and HOMO orbitals are also visualized in figure 9b and figure 9c respectively.

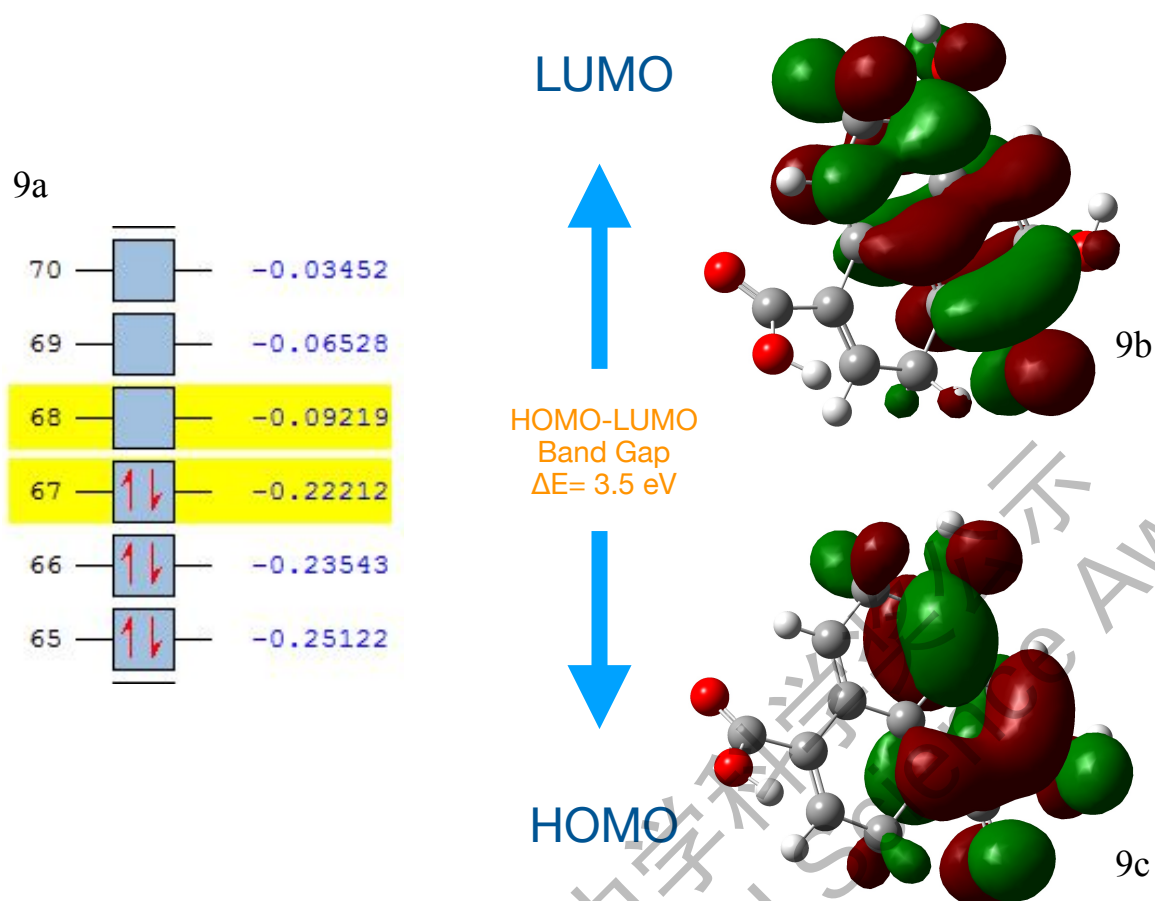


Fig 9, Calculated Orbitals and Band Gap. (a) The Calculated Orbitals including highlighted HOMO and LUMO; (b) Molecular Orbital Visualization for LUMO; (c) Molecular Orbital Visualization for HOMO

Lastly, the total electron density of the molecule is visualized, with the Electrostatic Potential (ESP) mapped onto it (Figure 10). This result may help to elucidate the electron transfer mechanism in the photocatalysis process of the CQD. [12]

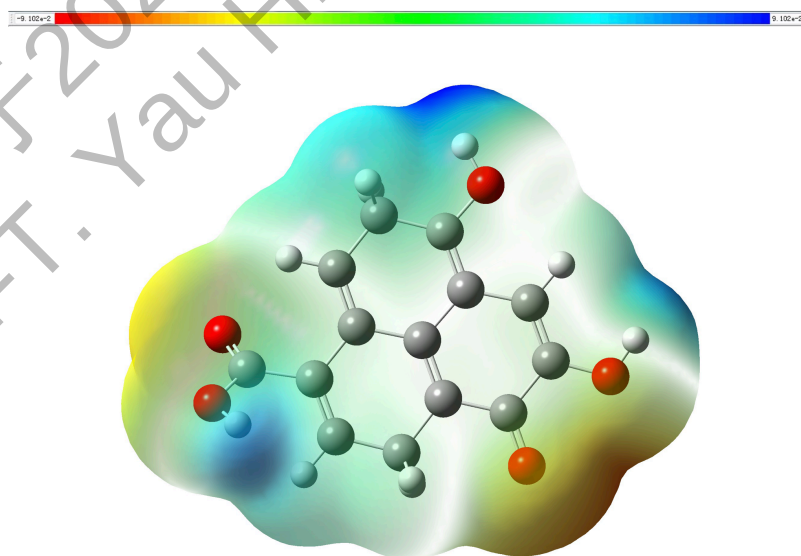


Fig 10, The electron density distribution with mapped ESP from DFT calculations.

4. Conclusion

In summary, in this study, CQDs are successfully prepared from table sugar using a microwave-assisted top down approach. The samples are characterized using FTIR and UV-Vis spectroscopy, and a model of the CQD is successfully proposed based on the characterization results. DFT calculations are performed on the model, confirming the accuracy of the model. The DFT results also reveals more properties regarding the molecular orbitals, dipole moment, optimized geometry, band gap, and electron density of the molecule. This research makes it possible to conveniently synthesize carbon quantum dots in an environmental friendly way. It also provides valuable characterization results both experimentally and theoretically. Lastly, the theoretical model presented helps model the structures and explain the properties of CQDs, setting the foundation for further studies on predicting the mechanism and optimizing the structures of carbon quantum dots.

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6. Appendix

The following files are raw data files from the Gaussian DFT computations attached in the additional files section. Here is a comprehensive guide to the files.

cqd_input.gjf	The input file of the proposed CQD molecular model before the optimization calculations (see 3.4).
opt_cqd.log	The output file from the DFT optimization calculations as described in 3.5.
freq_cqd.log	The output file from the DFT frequency calculations as in section 3.6
ir_cqd.txt	The IR peak values from the frequency calculations.
orbitals_cqd.txt	The calculated molecular orbitals and their respective energies of the CQD model.

致谢

本课题选题来源于作者所阅文献及在家中的动手尝试。论文整体由 Jonathan Xufeng Hu 撰写、杨敏老师修改。实验部分为Jonathan Xufeng Hu 在杨敏老师指导下完成。计算部分为Jonathan Xufeng Hu 在刘佳龙老师指导下完成。论文指导老师均为作者校内化学教师，指导为无偿指导，协助进行论文修改、协调实验操作、计算运行等指导。

感谢曹宵鸣教授、吕祖元同学提供计算部分所需计算资源。

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