New Perspectives in Science Education

International Conference
NEW PERSPECTIVES in SCIENCE EDUCATION

# Variation of the Synthesis for Influencing the Optical Properties of Carbon Quantum Dots

**Malte Petersen**[1], **Timm Wilke**[1*]

Carl von Ossietzky Universität Oldenburg,
Institute for Chemistry, Chemistry Education Department,
26129 Oldenburg, Germany[1]

## Abstract

*Quantum dots represent a novel and innovative class of nanomaterials, enabling precise adjustments in their absorption and emission properties. Their potential is evident in applications like phosphors and display technologies. The awarding of the Nobel Prize in Chemistry in 2023 has increased the general awareness of quantum dots, making the term familiar to many. From an educational standpoint, the introduction of these advancements into school curricula presents a valuable opportunity, allowing for the development of relevant experiments for educational purposes. The synthesis of zinc oxide quantum dots and carbon quantum dots is already achievable in educational settings.*

*In order to delve deeper into this subject, we suggest an alternative method of synthesis using a standard microwave. This method involves altering the ratios of reactants showcasing how these changes can influence the optical properties of the quantum dots. This approach not only highlights the important chemistry concept of structure-property relationships but also serves as an engaging introduction to the fields of spectroscopy and photochemistry.*

**Keywords:** *carbon quantum dots (CQDs), nanomaterial, optical properties, spectroscopy*

## 1. Introduction

The field of nanochemistry and nanotechnology encompasses a wide range of topics and is an integral part of our society. Its applications span various domains, including food chemistry, medicine, and electronics [1]. The impact of these technologies was underscored by the Nobel Prize in Chemistry 2023. The Nobel Committee recognized the significance of quantum dots in laying the groundwork for nanotechnology. The importance of this field has also been acknowledged by the Conference of Ministers of Culture (Kultusministerkonferenz) in Germany. In 2020, they included nanotechnology in the German national educational standards. As a result, this topic will soon be incorporated into the curricula of all German states.

Given this context, there is a clear need for effective experiments to support chemistry teachers in achieving their educational objectives. Several preliminary publications aiming to assist nanotechnology's implementation in schools include the synthesis of zinc oxide quantum dots [2] and targeted drug delivery enabled by nanoparticles [3], just to give two examples. Many other established experiments rely on the synthesis of nanoparticles using various d-block transition metals [4,5]. These are generally considered environmentally harmful and pose a risk to our ecosystem when released in larger quantities. As an alternative, carbon quantum dots (CQDs) have emerged in research as an alternative class of materials. They are currently being investigated, particularly in the context of Green Chemistry [6] or photochemical applications [7]. CQDs therefore offer great potential for transferring current research effectively into schools. Concepts relevant to teaching chemistry such as absorption, emission, or synthesis of nanoparticles can be taught using this class of nanomaterials. In school education, however, the topic is up to this time only barely represented. In this work, we will show a simple synthesis approach for realizing fluorescent CQDs. For this purpose, a commercially available microwave is used as a reactor and the fluorescence properties of the product are influenced by varying the reactants.

## 2. Scientific Background

Carbon quantum dots are a class of materials with unique properties based on carbon nanomaterials. They consist of various clusters of carbon atoms including other heteroatoms such as nitrogen, oxygen, sulfur, or phosphorus. Typically, the size of these clusters is less than 10 nm. Their most characteristic properties include good photoluminescence, high chemical adaptability, and being nontoxic to the environment [8].

CQDs are synthesized using two approaches (Fig. 1): The top-down and the bottom-up method [9]. In the top-down method, larger carbon-containing materials (bulk) such as carbon nanotubes, graphene or plants are broken down into smaller fragments. This can be carried out by burning or electrochemically treating the carbon base. In contrast, the bottom-up method synthesizes CQDs from smaller, molecular precursors such as atoms, organic molecules, or polymers. These precursors can be converted into clusters and then into CQDs by various chemical processes such as hydrothermal treatment or microwave pyrolysis. This second synthesis approach offers more precise control over the size and properties of the particles' surface.

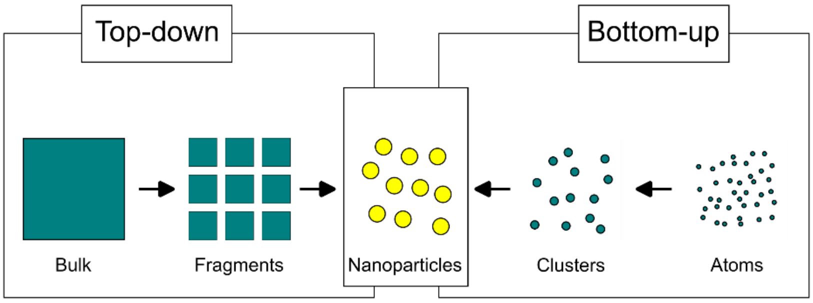

Fig. 1: Schematic representation of the top-down and bottom-up approaches for the synthesis of nanoparticles.

In bottom-up synthesis with the aid of a microwave, the treated solution is heated by microwave radiation. This results in rapid heating of the precursors which in turn results in a pyrolysis in which organic compounds are broken down and small carbon clusters can form in the solution. These serve as nuclei for the formation of CQDs. The resulting carbon cluster continues to grow through the integration of further carbon atoms. By adding different chemicals, the surface can be functionalized and the size and stability of the CQDs can be controlled. The exact mechanism varies across different syntheses using a microwave. In general, it is associated with improved reaction efficiency, shortened synthesis time, and the formation of CQDs with desirable optical and chemical properties. Following the reaction, the CQDs must be isolated from remaining impurities for further use. Typical methods here are dialysis, size exclusion chromatography, centrifugation, or the use of a separating funnel.

The photoluminescence properties of CQDs depend on their structure. CQDs have a crystalline core structure and various amorphous functional groups on the surface. The energy gap of the π-electron system in CQDs has a sufficient band gap to exhibit photoluminescence properties. The functional groups on the surface can also contribute to influence the light phenomenon. The targeted synthesis of CQDs allows them to emit light across the entire spectrum [10], with the coloration depending on the surface defects (broken bonds). Due to the oxidation processes that take place and the organic nature of the precursors, the hydroxyl group (-OH) is the most common functional group to influence this photochemical property [11].

## 3. Experimental Setting

The following procedure describes a simple synthesis of CQD dots for chemistry education in school, school laboratories or undergraduate laboratory courses. The experiment can be conducted in two variants, resulting in CQDs with different appearance and photoluminescence.

**Equipment:** 500 mL beaker, 100 mL beaker, 50 mL beaker, standing cylinder, glass rod, pipette, scale, spatula, microwave, UV/vis photo spectrometer, UV permeable cuvette, centrifuge, centrifuge tube, hotplate

**Chemicals:** urea, citric acid monohydrate (GHS07), demineralized water

**Optional:** separating funnel, dichloromethane (GHS 06, 07), ethanol (GHS 02, 07)

**Experiment:** For the synthesis of the CQDs, citric acid (3 g, 14.2 mmol) is dissolved with urea (variant A: 1 g, 16.6 mmol, variant B: 3 g, 50 mmol) in 8 mL demineralized water in a 50 mL beaker. The clear solution is then transferred to the 500 mL beaker and placed in the middle of the microwave. The microwave is operated at 700 W for 10 min until a black, dry residue has formed in the beaker. The resulting product is taken up in 30 mL of demineralized water and centrifuged for 1 h at 8.000 rpm. A clear, light-yellow solution is pipetted off and can be analyzed for its absorption properties. For longer-term storage of the CQDs, they can be isolated by evaporating the water on a hotplate.

If no centrifuge is available, one alternative for the school is to shake out the CQDs with the help of a separating funnel. For this, the product is taken up after in 30 mL of demineralized water after microwaving and poured into the separating funnel with a 1:2 mixture of ethanol:dichloromethane. This procedure requires working under a fume hood and wearing gloves. The CQDs in the organic phase can be isolated again by evaporating the organic solvents and then be stored.

## 4. Observations and Results

In this experiment, urea and citric acid are used for the microwave-assisted synthesis of CQDs [12]. As can be seen in Fig. 2, the synthesized CQDs differ in their appearance and photoluminescence behavior. The preparation with the 3:1 ratio (variant A) is yellowish in ambient light whereas the 1:1 synthesis (variant B) is from a dark yellow to almost brownish appearance. Under the irradiation of ultraviolet light (λ = 365 nm), the difference is even more visible. Here a color difference from blue (3:1, A) to light yellow (1:1, B) can be observed.

Fig. 2: Photography of the synthesized CQDs with a ratio of 3:1 (left) and 1:1 (right) citric acid and urea. The photo on the left was taken in ambient light and on the right under UV light (λ = 365 nm).

To understand this observation, urea must be understood as the variable that changes during synthesis. The presence of urea as a precursor in the process affects the optical properties and fluorescence of the CQDs [13]. Both the observation with the naked eye and the recorded absorptions confirms this as can be seen in Fig. 2 and 3.

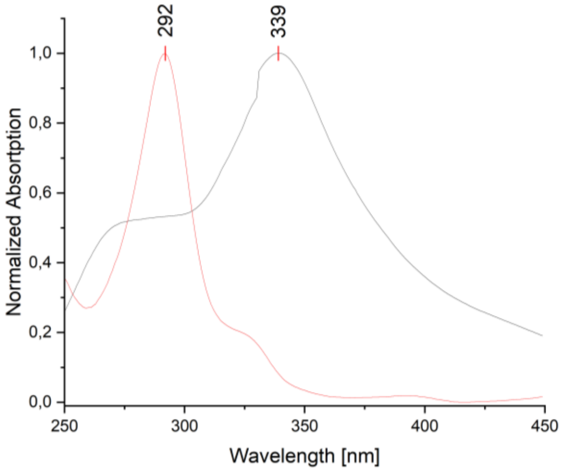

Fig. 3: Normalized absorption spectra of synthesis with a ratio of 3:1 (red) and 1:1 (grey) citric acid and urea (the graph jump at 330 nm can be explained by the UV/vis lamp switch).

In the normalized absorption spectra a bathochromic effect, a shift of the absorbance into the longer wavelength range, from the 3:1 synthesis (red curve) to the 1:1 synthesis (gray curve) can be seen. This ranges from 292 nm to 339 nm and amounts to 47 nm. The visible fluorescence depends on the characteristics of the surface of the CQDs [11]. It can therefore be assumed that varying the amount of urea compared to citric acid influences the photoluminescence of the CQDs. It is reported that the proportion of hydroxyl groups on the surface can be influenced by urea [13]. An increase in surface groups like these leads to increased passivation of the surface of the CQDs, which causes the bathochromic effect [11].

## 5. Conclusion and Outlook

In this article, a simple method for the synthesis of CQDs is presented. The method is easy, safe to conduct, and has a high probability of success. The effects are impressively visible, particularly concerning the change in fluorescence. Furthermore, it gives the students an insight into what at first glance appears to be an unconventional synthesis method in current research. The observed bathochromic shift in absorption and the change of the fluorescence provides a starting point for investigating the material properties of CQDs as nanomaterials. This initial approach can be researched further and adapted for use in schools or universities. Here, for example, the use as a catalyst for classic organic reactions lends itself to demonstrating the diverse advantages of this material class. Another possibility is the investigation of their photochemical properties. These could be used to simulate the photochemical degradation of pollutants such as drugs by degrading a model dye. It also seems possible that CQDs can be used in school for a greener approach to photochemical hydrogen generation. This would allow a reference back to current topics relating to the future energy supply and the discussion of hydrogen as an energy carrier. This brief list already shows that CQDs are a new class of materials for schools, which offers potential for a possible implementation in regular school operations in various areas.

## Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG) for funding this work through the Sonderforschungsbereich/Transregio 234 CataLight, project number 364549901 (project Ö1).

## References

[1] Dan, D. T. (2020). Nanotechnology, Nanoparticles and Nanoscience: A New Approach in Chemistry and Life Sciences. SNL **10**/02, 17–26.

[2] Wilke, T., Waitz, S., von Hoff, E., Waitz, T. (2018). Farbig fluoreszierende Zinkoxid- Nanopartikel. CHEMKON **25**/1, 16–22.

[3] Fruntke, A., Behnke, M., Stafast, L. M., Träder, T., Dietel, E., Vollrath, A., Weber, C., Schubert, U. S., Wilke, T. (2023). Targeted Drug Delivery: Synthesis of Smart Nanocarriers for School Chemistry Education. J. Chem. Educ. **100**/2, 751–759.

[4] Parvizian, M., Bechter, J., Huber, J., Chettata, N., Roo, J. de (2023). An Experimental Introduction to Colloidal Nanocrystals through InP and InP/ZnS Quantum Dots. J. Chem. Educ. **100**/4, 1613–1620.

[5] Landry, M. L., Morrell, T. E., Karagounis, T. K., Hsia, C.-H., Wang, C.-Y. (2014). Simple Syntheses of CdSe Quantum Dots. J. Chem. Educ. **91**/2, 274–279.

[6] Dandia, A., Saini, P., Sethi, M., Kumar, K., Saini, S., Meena, S., Meena, S., Parewa, V. (2021). Nanocarbons in quantum regime: An emerging sustainable catalytic platform for organic synthesis. Catalysis Reviews, 1–55.

[7] Syed, N., Huang, J., Feng, Y. (2022). CQDs as emerging trends for future prospect in enhancement of photocatalytic activity. Carbon Lett. **32**/1, 81–97.

[8] Giordano, M. G., Seganti, G., Bartoli, M., Tagliaferro, A. (2023). An Overview on Carbon Quantum Dots Optical and Chemical Features. Molecules (Basel, Switzerland) **28**/6.

[9] Das, R., Bandyopadhyay, R., Pramanik, P. (2018). Carbon quantum dots from natural resource: A review. Materials Today Chemistry **8**, 96–109.

[10] Bao, L., Liu, C., Zhang, Z.-L., Pang, D.-W. (2015). Photoluminescence-tunable carbon nanodots: surface-state energy-gap tuning. Advanced materials (Deerfield Beach, Fla.) **27**/10, 1663–1667.

[11] Shabbir, H., Csapó, E., Wojnicki, M. (2023). Carbon Quantum Dots: The Role of Surface Functional Groups and Proposed Mechanisms for Metal Ion Sensing. Inorganics **11**/6, 262.

[12] Wang, Y., Godin, R., Durrant, J. R., Tang, J. (2021). Efficient Hole Trapping in Carbon Dot/Oxygen-Modified Carbon Nitride Heterojunction Photocatalysts for Enhanced Methanol Production from CO2 under Neutral Conditions. Angewandte Chemie (International ed. in English) **60**/38, 20811–20816.

[13] MS, J., Nambiar, A., A, S. (2023). Modulating the fluorescence properties of carbon dots by varying the stoichiometric ratios of citric acid and urea during the synthesis. Materials Today Communications **37**, 107199.