BLUE AND GREEN EMITTING CARBON DOTS EMBEDDED IN SiO_2 MONOLITH GLASS – ANALYSYS OF OPTICAL PROPERTIES

KATARZYNA HALUBEK-GLUCHOWSKA*, ROBERT TOMALA, ANNA LUKOWIAK

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okolna 2, 50-422 Wroclaw, Poland
**Corresponding author: K.Gluchowska@intibs.pl*

Carbon dots (CDs) have been extensively studied as an alternative to quantum dots, semiconductors, and rare-earth-element-doped structures due to their non-toxic and metal-free optical properties [1,2]. In medicine, they have potential applications in drug delivery systems, diagnostics, and sensing [3]. A composite material based on glass and carbon dots can be effectively utilized in biomedical applications as an optical marker or biosensor. The aim of our research was to produce SiO_2 glass monoliths doped with blue or green luminescent carbon dots (bCDs/gCDs) to investigate their optical properties.

Morphology and structure of CDs

Blue carbon dots (bCD) were prepared through low-temperature pyrolysis of citric acid in the presence of ammonia water, while urea was used instead for the synthesis of green carbon dots (gCD). Structural and morphological analyses (XRD, TEM, IR) were conducted on the obtained CDs, which were subsequently used as luminescent labels in the SiO_2 glass matrix. The morphology of the dots was analyzed using transmission electron microscopy (TEM), revealing an average size of approximately 4 – 7 nm in diameter. The bCDs were spherical in shape and did not aggregate, in contrast to the gCDs (Fig. 1), which had a tendency to aggregate and have around 20 – 50 nm in length.

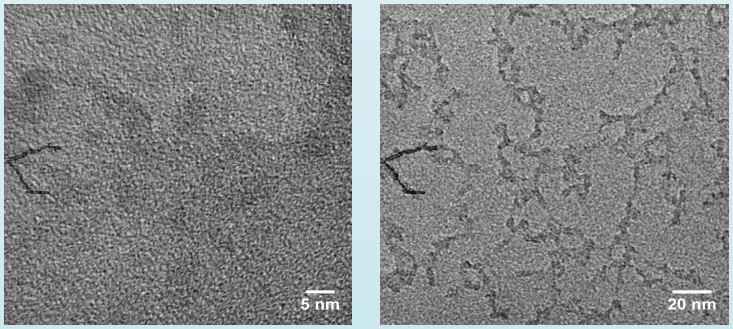

Figure 1. Transmission electron microscope (TEM) images of bCDs (left) and gCDs (right).

In the diffraction pattern (Figure 2) for both structures, a broad reflection is observed at approximately 15–25° 2θ, corresponding to the reflection of radiation between the sp^2 planes of the graphene structure. For the gCDs, an additional peak appears around 27° 2θ, indicating the presence of a crystalline structure characteristic of graphite (multilayer graphene structure). These diffractograms confirm the carbon-based nature of the carbon dot core, which allows for the attachment of various functional groups.

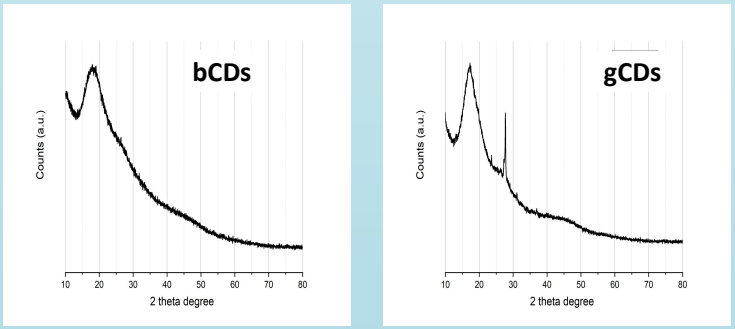

Figure 2 . X-ray diffraction patterns of bCDs / gCDs.

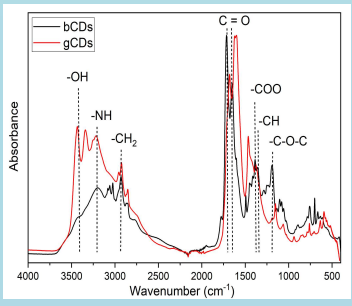

Figure 3. Infrared spectra of bCDs / gCDs.

To identify the functional groups present on the surface of the bCDs or gCDs, infrared spectroscopy (FTIR) measurements were performed (Figure 3). The FTIR spectra revealed the presence of vibrations corresponding to the following functional groups: -OH (~2600~3430 cm^{-1}), -NH (3195 cm^{-1}), $-CH_3$ (2940 cm^{-1}), -COOH (1720–1360 cm^{-1}), C–O–C (1185 cm^{-1}) C–N (1080cm^{-1}).
The analysis of the IR spectrum for the dots indicated that the gCD dots have a significantly higher number of amine groups on their surface, which may greatly influence their luminescence color.

Optical properties of CDs and SiO_2 monoliths labeled with CDs

SiO_2 monoliths with bCD/gCD were prepared using the sol-gel method with Tetraethoxysilane (TEOS). Carbon dots (bCD/gCD) were added to the prepared solution and stirred for 2 hours. The mixture was then poured into containers and dried at 37 °C for 24 hours, followed by an 8-week drying period to ensure complete evaporation of water. After drying, monoliths of different colors were obtained (Figure 4), which exhibited luminescence in various colors under UV (365 nm) illumination.

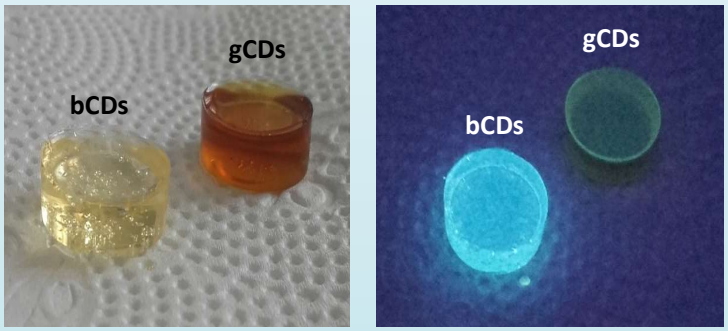

Figure 4. SiO_2 monoliths with bCDs/gCD under VIS (left) and UV (right) illumination.

For both types of CDs, the emission color is strongly dependent on the excitation wavelength (Figure 5). This is likely due to the presence of various functional groups on the dots surface, where excitation at different wavelengths results in different colored luminescence. It can be observed that for both types of dots, excitation in the range of approximately 300–350 nm leads to emission in two ranges, with the emission band potentially comprising two or more peaks. This may suggest that the absorption bands of different functional groups overlap in this range. Additionally, shifts and broadening of the emission bands are observed for the CDs-doped glasses compared to the dots themselves.

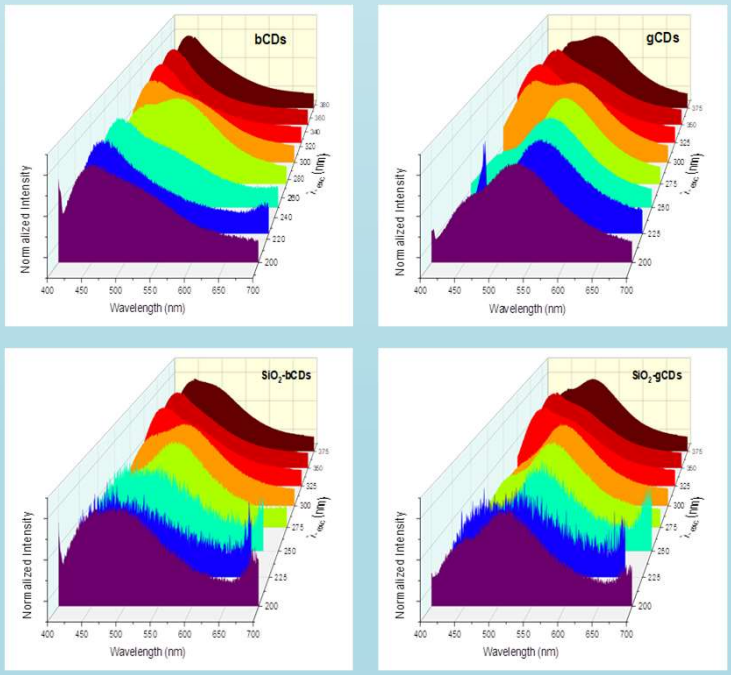

Figure 5. Emission spectra of bCDs (top left), gCDs (top right), and glasses labeled with them (bottom) as a function of excitation wavelength

Conclusions:

- The size of the dots, their degree of aggregation, their amorphous or crystalline structure, and, most importantly, the presence of additional functional groups such as amino groups on the surface of carbon dots, have a significant impact on their luminescent properties.
- When carbon dots (CDs) are embedded in a SiO_2 matrix, the surface functional groups of the CDs can interact with the silica network. This interaction can alter the electronic environment around the luminescent centers of the carbon dots. Such changes often result in broadening and shifting of the emission bands
- Control over the parameters of dot synthesis and glass preparation allows for precise design and modulation of the spectroscopic properties of these structures, making them suitable for a wide range of applications.

References:

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[2] Qu D. et al., Scientific Reports, 2014, 4, 5294
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Acknowledgment

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