Green Emissive Carbon Dots: Controlled Synthesis and Enhanced Properties Using Mesoporous Silica Matrices

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In recent years, there has been an intensive effort to replace semiconductor quantum dots and rare-earthbased materials in optoelectronics and photonics with environmentally friendly and cost-effective alternatives. Carbon Dots (CDs) have emerged as a promising candidate due to their efficient and tunable emission properties, ease of chemical functionalization, surface passivation, chemical inertness, resistance to photobleaching, and biocompatibility.

This study[1] employs a static open-air oven synthesis method to investigate CDs synthesized within solidstate matrices of commercially available mesoporous silica. The photophysical properties of these solid-state hybrids were compared with those of reference CDs prepared without silica matrices and dispersed in water.

We performed a bottom-up synthesis using citric acid and urea as precursors, which assembled within two different silica matrices, namely commercial MCM-48 and SBA-15, forming two distinct carbon dots-silica hybrid systems. The structural and optical properties of these hybrids were characterized using techniques such as Transmission Electron Microscopy (TEM), Attenuated Total Reflectance (ATR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), UV-Vis spectroscopy, as well as steady-state and time-resolved photoluminescence (PL).

Within the silica matrices, we observed changes in the optical properties of the CDs compared to those dispersed in water, specifically noting an increase in the green emissive band relative to the blue band. The interaction between the CDs and the silica matrix was further confirmed by studying the effects of irradiation on the hybrids over time, which resulted in an overall increase in green luminescence intensity. XPS measurements revealed a higher degree of doping, favoring the formation of different types of nitrogen dopants at the expense of pure aromatic systems. TEM images, obtained after extracting the CDs from the host matrix, indicated that silica acts as an effective nanoreactor, controlling the size and distribution of the particles.

The synthesis of CDs within a silica environment facilitated better control over nanoparticle size and led to the production of more green-emitting centers. In contrast, synthesis outside of the silica matrix resulted in less size control and higher production of blue-emitting channels. Further investigation into the luminescence properties in these two environments revealed that in silica, the emission is primarily attributed to surface centers. This interaction with the matrix is enhanced by irradiation but can be hindered by molecular aggregation-induced quenching. Conversely, in water, the emission is predominantly due to molecular centers. Overall, this study highlights the advantages of using mesoporous silica matrices to control the synthesis and photophysical properties of carbon dots, paving the way for more green and inexpensive materials in optoelectronics and photonics. MACCS1 - 1st Italian Chinese Swedish workshop on "Modeling and Characterization of Complex Systems"



Figure 1 – Schematic model of the photoluminescence interaction of a carbon dot with water and silica environments under UV light [reproduced from ref 1, copyright Elsevier 2022].

REFERENCES

[1] Olla C., Ricci P.C., Chiriu D., Fantauzzi M., Casula M.F., Mocci F., Cappai A., Porcu S., Stagi L., Carbonaro C.M. (2022) "Selecting Molecular or Surface Centers in Carbon dots-silica Hybrids to Tune the Optical Emission", *Journal of Colloid and Interface Science*, 634, 402-417. https://doi.org/10.1016/j.jcis.2022.12.023