How Carbon Dots Shine: Multiscale Modeling of Carbon Dots

Michal Otyepka[1,2]

[1] CATRIN, Palacký University Olomouc, Czech Republic, michal.otyepka@upol.cz
[2] IT4Innovations, VSB–Technical University of Ostrava, Czech Republic

Carbon dots (CDs) are among the most promising carbon-based nanomaterials owing to their bright and tunable photoluminescence (PL), high photostability, low toxicity, excellent biocompatibility, and broad application potential in sensing, bioimaging, optoelectronics, and photocatalysis. Despite more than two decades of intensive research, the relationship between their structure and optical properties remains poorly understood because CDs are inherently heterogeneous systems comprising carbonized domains, molecular fluorophores, surface functional groups, and self-assembled supramolecular motifs. Consequently, the origins of their PL and photocatalytic behavior remain subjects of active debate [1,2].

To address these challenges, we have developed a multiscale computational framework that combines quantum-chemical calculations, classical and reactive molecular dynamics (MD) simulations, QM/MM methodologies, and data-driven molecular model construction. Using ab initio calculations, we investigated the reaction mechanisms governing CD formation from simple precursors such as citric acid and ethylenediamine, identifying thermodynamically and kinetically feasible pathways consistent with experimental observations [3]. Reactive MD simulations provide further insight into intermediate structures formed during later synthesis stages, while classical all-atom MD simulations reveal the structural organization of CDs and the localization of molecular fluorophores generated during synthesis [4,5].

The resulting molecular models were subsequently employed to investigate the photophysics of CDs. We demonstrate how molecular fluorophores such as 5-oxo-1,2,3,5-tetrahydroimidazo[1,2-a]pyridine-7-carboxylic acid (IPCA), polycyclic aromatic hydrocarbons, and their supramolecular assemblies contribute to absorption and emission processes. Quantum-mechanical and hybrid QM/MM calculations reveal how dimerization, self-assembly, noncovalent interactions, and confinement within the carbon-dot environment modify excited-state properties and photoluminescence. The simulations further uncover complex communication pathways between photoluminescent centers involving charge transfer, energy transfer, intersystem crossing, and environmental relaxation effects [6].

Recently, we extended this framework to non-carbonized CDs derived from citric acid and ethylenediamine, combining all-atom MD simulations, TD-DFT calculations, and photoluminescence quenching experiments [7]. This study showed that CA–EDA oligomeric condensation products containing IPCA units spontaneously assemble into dynamic approximately 2 nm nanoparticles with amorphous internal structures and fluorophore-rich stacked domains. TD-DFT calculations revealed that photoexcited species localize on spatially distributed IPCA-rich domains rather than being confined to a buried carbon core. Importantly, these emissive domains remain solvent-accessible, as confirmed by Hg^{2+}-induced PL quenching and lifetime shortening. This provides direct molecular-level evidence that accessible fluorophore-rich domains serve as active optical centers and interaction sites for sensing and photocatalytic processes.

Beyond explaining optical properties, the developed models provide a platform for understanding and optimizing the behavior of CDs in practical applications, including sensing and photocatalysis [8,9,10]. The presented studies demonstrate how physically grounded molecular models can bridge the gap between synthesis conditions, atomistic structure, excited-state localization, and functional performance. Such mechanistic insight is essential for moving from empirical synthesis toward the rational design of next-generation carbon dots with tailored optical, photocatalytic, and photochemical properties.

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