Designing Light-Driven Polymerisation Pathways Through Tailored Carbon Nanostructures for 3D Printing Applications

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The evolution of materials for photopolymerization has been driven by the need for precise, efficient, and tunable light-activated processes, spanning applications from coatings to advanced additive manufacturing. Conventional photoinitiators, while effective, are often limited by narrow absorption ranges, potential toxicity, and restricted tunability. As a result, increasing attention has been directed toward alternative, more versatile components that can operate under milder and more sustainable conditions. In this context, carbon dots (CDs) have emerged as a promising class of nanomaterials capable of addressing several of these challenges.

Carbon dots are nanoscale carbon-based structures distinguished by their rich and tailorable surface chemistry. Through careful selection of precursors and the introduction of heteroatoms, their optical and redox properties can be finely tuned. This tunability enables CDs to act as active components in photoinitiating systems, where they not only absorb light but also participate directly in the initiation process. Unlike traditional photoinitiators, CDs often exhibit multifunctional behavior, combining light harvesting with the ability to generate reactive excited states that can drive either radical or cationic polymerization mechanisms [1].

The practical relevance of CDs has been clearly demonstrated in photopolymerization processes used in modern 3D printing technologies. They can function as efficient photoinitiating components under visible light, enabling polymerization with improved control over kinetics and reduced reliance on conventional, often less sustainable photoinitiators [2]. This is particularly important in techniques such as digital light processing (DLP), where curing efficiency, spatial resolution, and material compatibility are critical. The incorporation of CDs into such systems not only enhances process performance but also enables the design of more environmentally friendly formulations. Beyond structural fabrication, CDs enable the development of functional printed objects, introducing additional functionalities such as photocatalytic activity or antimicrobial effects, thereby expanding their potential in transdermal drug delivery and biomedical applications.

A central aspect of CD behavior in photochemical systems lies in their ability to mediate energy and electron transfer processes, which are closely linked to the generation of reactive oxygen species (ROS). These include singlet oxygen and hydroxyl radicals, whose formation pathways depend on the electronic structure and surface functionalities of the CDs. Well-established photophysical principles indicate that subtle variations in surface groups and doping can shift the balance between energy- and electron-transfer mechanisms [3]. This level of control is particularly valuable in designing photopolymerization systems with tailored reactivity, as ROS can participate in or modulate initiation pathways, especially in hybrid or oxygen-mediated systems.

More broadly, the integration of carbon dots into photopolymerization systems reflects a shift toward designing materials that operate across multiple levels of complexity, in which performance arises from the interplay among structure, surface chemistry, and dynamic photophysical processes. CDs exemplify how relatively simple, sustainably synthesized nanomaterials can be engineered to perform sophisticated functions in technologically relevant systems. Their continued development is likely to play a significant role in advancing next-generation photoinitiating systems and expanding the capabilities of light-driven manufacturing technologies.

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REFERENCES

[1] Krok D, Tomal W, Knight AJ, Tartakovskii AI, Farr NTH, Kasprzyk W, Ortyl J, (2023) "Highly efficient carbon dot-based photoinitiating systems for 3D-VAT printing". *Polymer Chemistry*, 14, 4429–4444. DOI: 10.1039/D3PY00726J

[2] Tomal W, Świergosz T, Pilch M, Kasprzyk W, Ortyl J, (2021) "New horizons for carbon dots: quantum nano-photoinitiating catalysts for cationic photopolymerization and three-dimensional (3D) printing under visible light". *Polymer Chemistry*, 12, 3661–3676. DOI: 10.1039/D1PY00228G

[3] Yaemsunthorn K, Sysło A, Krok D, Kasprzyk W, Spiralewicz K, Pacia M, Thongpan W, Kobielusz M, Macyk W, Ortyl J, (2024) "Understanding photocatalytic processes in carbon dots with nitrogen and sulfur heteroatoms: Energy or electron transfer?". *Carbon*, 234, 119967. DOI: 10.1016/j.carbon.2024.119967