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Freeform Graphene Oxide-Quantum Dot Microstructures via Multiphoton Crosslinking

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Extended Abstract

Graphene has garnered much interest for its unique electronic, mechanical, and optical properties and it is composed of carbon atoms arranged in a two-dimensional (2D) regular hexagonal structure. Graphene oxide (GO) is the oxidization of graphene, is low-cost and has superior water solubility than graphene; as such, it has many potential applications [1]. Although GO contains more oxygen functional groups, which results in poor conductivity, it can be reduced by laser illumination and transformed into reduced graphene oxide (rGO) to raise its conductivity. Many research groups have adopted lasers with wavelengths ranging from ultraviolet to near-infrared to manufacture GO microelectronic patterns or devices on GO films. Nevertheless, certain graphene-based materials for application in the energy, environmental, sensing, and biological fields often require the assembly of 2D graphene sheets into three-dimensional (3D) architectures [2]. 3D microstructures can be achieved by two-photon photolithography, such as two-photon polymerization (TPP) or two-photon crosslinking (TPC), which use two photons with low molecular weight photoinitiators or photoactivators to trigger the respective polymerization reactions or crosslinking reactions. Two-photon excited photochemistry can be tightly confined inside the focal spot of a high numerical aperture (NA) objective on an ultrafast laser beam; hence, the desired 3D polymerized resin- and protein-crosslinked microstructures with subdiffraction-limited spatial resolution can be fabricated via the point-by-point scanning mechanism. 3D freeform polymer microstructures doped with GO nanosheets or single-wall carbon nanotubes have been fabricated to improve the mechanical and electrical properties of the polymer structure [3,4]. However, the GO in this application is only a guest material since the polymer is the host matrix.

In the present study, a graphene oxide-quantum dot (GOQD) aqueous solution with rose Bengal (RB) as the photoactivator can directly produce a pattern-like aggregation after patterned laser illumination. GOQD is near-zero dimensional with various types of defects at the basal plane. These defect sites can provide the exchange of carbon-oxygen at surface complexes and trap oxygen onto the edge or absorb them on the surface. This pattern-like aggregation phenomenon is similar to the TPC process of bovine serum albumin (BSA) when oxygen is necessary to initiate the photochemistry. This photon-induced GOQD assembly mechanism may occur through Förster resonance energy transfer (FRET) when the photoactivator (RB) as a donor chromophore transfers energy to triplet oxygen ($^3O_2$) as the acceptor chromophore, thereby transforming into singlet oxygen ($^1O_2$). Then, the singlet oxygen activates the GOQDs to produce free radicals that promote the photo-crosslinking among the GOQDs. Based on this photochemistry, 3D freeform GOQD-only microstructures with a resolution near the diffraction limit has been fabricated via TPC using RB as the photoactivator.

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