Hierarchical graphene quantum dot -copper nanocluster superstructures: Synergistic assembly for optical limiting application

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Supporting Information

S2p spectra of CUNC, GQD and the hybrid

CUNC exhibits a distinct $S2p_{3/2}$ at 161.81 eV characteristic of Cu-S bond[26] whereas GQD exhibits peaks at 161.21 eV and 163.3eV (dominant) characteristic of Sulphur doping (thiophenic sulphur) in the graphene basal structure. In the case of hybrid these separate peaks are replaced by a single composite peak at 162.9 eV. This spectral convergence indicates a significant electronic interaction at the hybrid interface. The presence of higher binding energy components (~166-168 eV) in both the pure clusters and the hybrid, attributable to oxidized sulfur species (e.g., disulfides and sulfonates), indicates that the EDC-NHS reaction did not induce significant additional oxidation. In summary, the XPS data collectively demonstrate: (i) the consumption of carboxylic acid groups on the GQDs (ii) the consumption and changed environment of amine groups from the glutathione ligands, and (iii) the preservation of the core of the cluster in spite of the ligand rearrangement during the cluster formation. These findings offer definitive proof of the successful synthesis of a covalent linked N, S-GQD-CUNC hybrid material via EDC-NHS coupling.

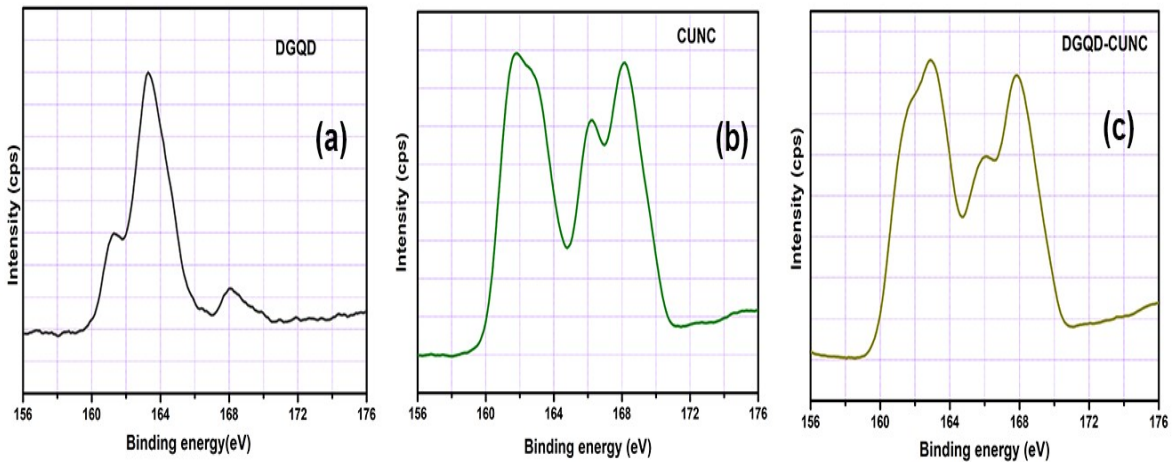

Figure S1: (a) S2p spectra of DGQD (b) S2p spectra of CUNC hybrid (c) S2p spectrum of DGQD-CUNC hybrid

TEM images of graphene quantum dots

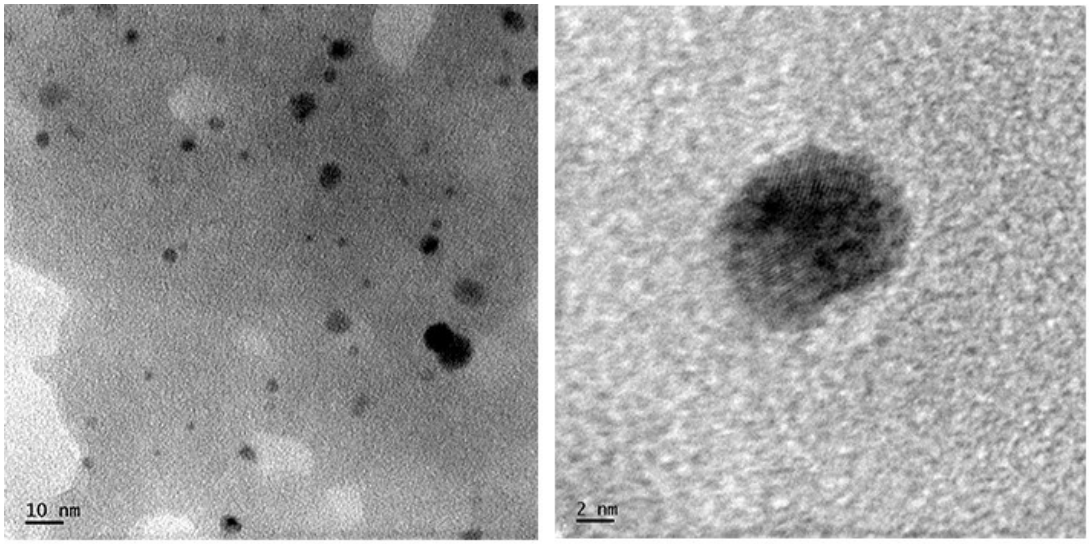

Figure S2: TEM and HR-TEM images of images synthesized N-S graphene quantum dots

Samples photographs used for Physico-chemical characterizations

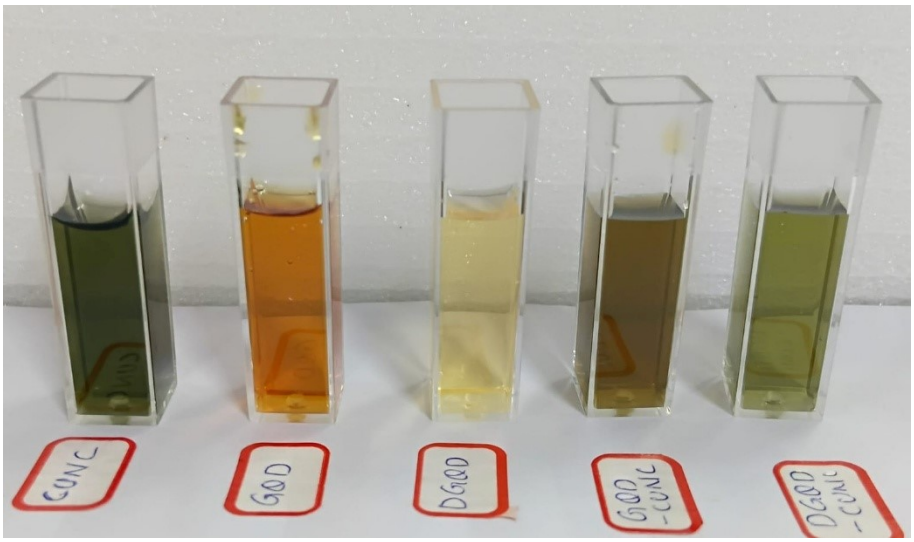

Figure S3: The photograph of the physical samples used for NLO studies