Enhanced photoluminescence of gamma-irradiated S, N graphene quantum dots

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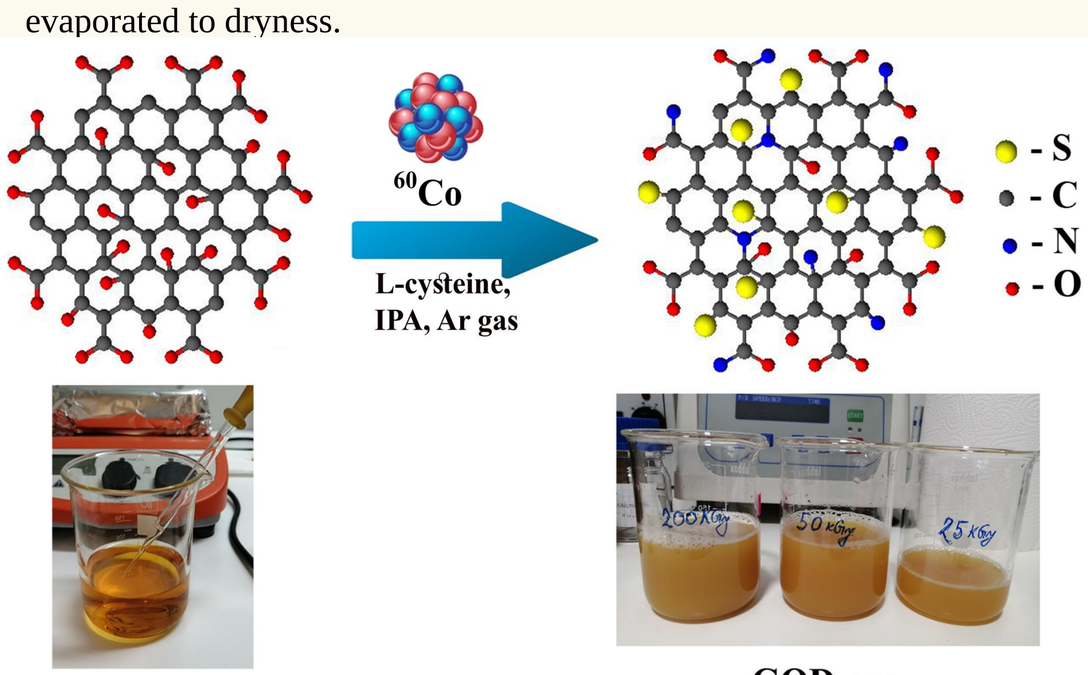
ABSTRACT

In this study, we present a simple, one-step method for functionalization of GQDs with gamma irradiation in the presence of amino acid L-cysteine as an S, N heteroatom donor and isopropyl alcohol as a radical scavenger. The successful doping of S and N atoms was confirmed with FTIR spectroscopy while AFM and DLS measurements showed an increase in particle diameter of modified GQDs. After gamma irradiation, the improvement in photoluminescence quantum yield (QY) was noticable in all samples especially for sample irradiated with a dose of 25 kGy.

EXPERIMENTAL

In water dispersion of GQDs, synthesized electrochemically, we added 1 vol% isopropyl alcohol and 2 mass% of L-cysteine. The mixture was purged with Ar gas for 15 minutes and then exposed to Co-60 nuclide as an irradiation source. The applied doses of gamma irradiation were: 25, 50 and 200 kGy. After irradiation, the samples were dialyzed for two days and evaporated to dryness.



CONCLUSION

The successful incorporation of S and N heteroatoms in GQD structure was achieved by avoiding aggressive chemical reagents.
With S, N doping the analysis showed that the optical and morphological properties of GQDs improved. One of the most significant improvements is in photoluminescence quantum yield which is several times higher compared to unmodified GQDs.

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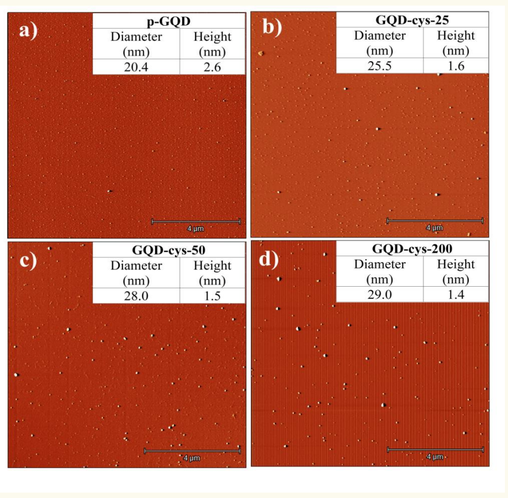
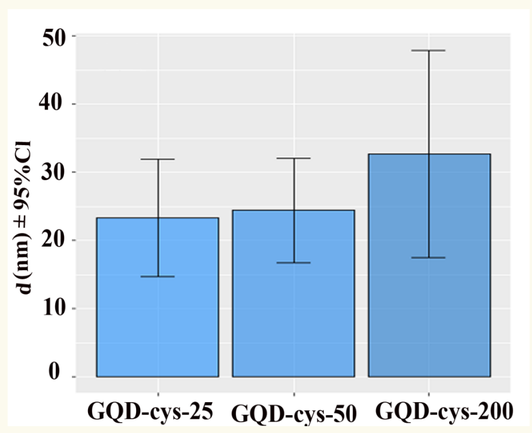
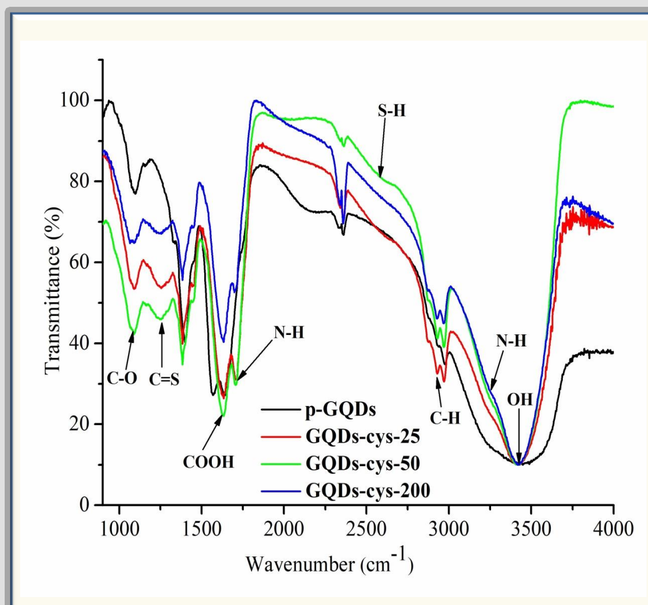
RESULTS AND DISCUSSION

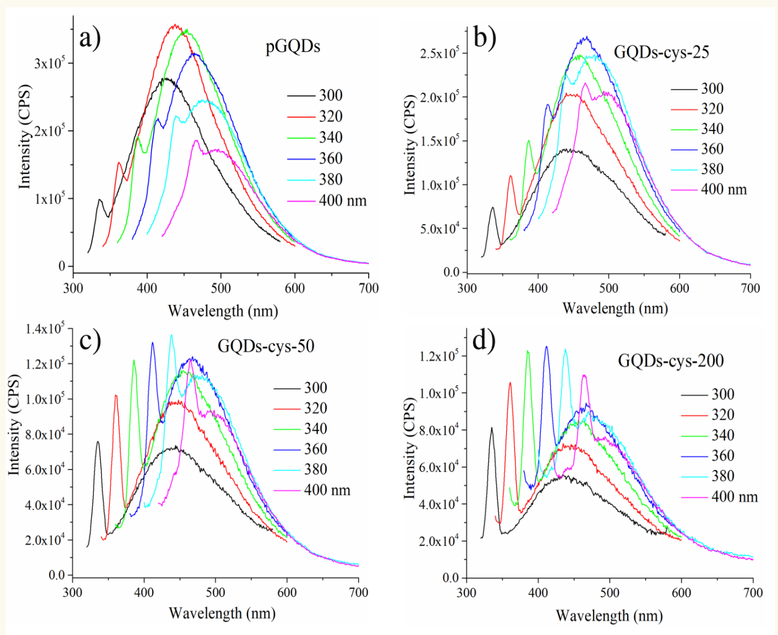




Both AFM and DLS measurements were in a good correlation and indicated that gamma irradiation increased the layer separation and overall particle diameter of GQDs. The average diameter ranged from 25 nm up to around 30 nm for irradiated samples and for non-irradiated p-GQDs diameter was 20 nm.



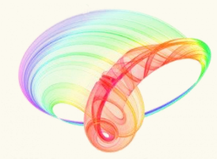
As it can be seen, FTIR spectra showed the successful incorporation of S and N heteroatoms in the structure of irradiated GQDs. Sulfur binding was achieved through S-H and C=S groups detected at around 2550 cm^{-1} and 1250 cm^{-1}, respectively while peaks at approximately 3250 and 1700 cm^{-1} stems from N-H stretching vibrations. The spectra also indicated that the aromatic structure of GQD-cys was preserved after irradiation.



From both irradiated and non-irradiated PL spectra of GQDs the maximum of emission band is shifted under the excitation wavelengths from 300 to 400 nm. This optical behavior is very common in GQDs and explains with size-dependent quantum confinement effects, surface functional groups, etc.
The center of emission for p-GQDs was shifted from 426 nm to 496 nm (from indigo to blue) while irradiated GQDs showed emission mostly in the range from 440-495 nm (blue emission).
For p-GQDs the highest absorption intensity was detected at 320 nm wavelength and in the case of irradiated GQDs this absorption maximum was at 360 nm.
PL quantum yield also improved after the functionalization. The best result was achieved for the sample irradiated with 25 kGy dose (Table 1). For this sample PL QY was 15 times higher compared to non-irradiated p-GQDs, and around 7 times higher up against other irradiated samples.

Sample	QY (%)^{360nm}
p-GQDs	1.45
GQD-cys-25	21.60
GQD-cys-50	5.15
GQD-cys-200	3.12
Rhodamine B	31

Table 1. PL quantum yield at excitation wavelength 360 nm



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