

# Opto-electrical characteristics of PEGylated carbon quantum dots

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## Abstract

Carbon quantum dots, the last member of carbon nanomaterials, owing to their strong and non-bleaching photoluminescence combined with low toxicity and easy conjugation, are acknowledged to be viable counter candidates of semiconducting quantum dots for biology and medicine applications. In order to assess the potential contribution of these materials to other fields than biology, throughout this article we have investigated the optical and electric behavior of two types of PEGylated carbon quantum dots. The article will present both the synthetic routes and photophysical properties, in addition to the electrical measurements achieved on metallic interdigitated electrodes.

The material we have investigated, namely carbon quantum dots, were prepared by (i) laser ablation of graphite and subsequently passivation with diamine-terminated oligomeric polyethylene glycol (PEG<sub>1500N</sub>), denoted CQD-PEG1500N [1] and (ii) microwave assisted hydrothermal method having as precursor glucose based water solution [2] and subsequently passivation with poly(ethylene glycol) bis (carboxymethyl) ether (PEG600), denoted CQD-PEG600.

Photophysical characterisations revealed low photoluminescence of self passivated CQD (carbon quantum dots obtained by microwave assisted hydrothermal decomposition of glucose) due to the quenching effect of oxygen rich functional moieties on their surface (epoxy, hydroxyl, and carboxylic groups), but the photoluminescence has greatly increased after polymer passivation (for instance the QY of CQD-PEG1500N is 5% at 440 nm excitation while the photoluminescence of the CQD before passivation is undetectable). Structural studies revealed a size distribution ranging from 2 to 6 nm for the CQD-PEG1500N and 3-4 nm for CQD-PEG600. In addition, HR - TEM characterization confirmed the crystalline structure of the CQD core in all of the carbogenic nanomaterials synthesized in this study, a representative TEM image of CQD-PEG1500N is shown in Fig.1.

Photoluminescence (PL) dependence on excitation wavelength in this carbogenic nanomaterial dispersed in chloroform is presented in Fig.2 and is a result of its heterogeneous electronic structure present in the sp<sup>2</sup> domains. While the maximum intensity of self passivated CQD and CQD-PEG600 was observed at 380 nm, the CQD-PEG1500N exhibited the highest photoluminescence at 420 nm. Based on those photoluminescence maxima, the optical band gap ( $E_{g\text{ opt}}$ ) of self passivated CQD, CQD-PEG600, and CQD-PEG1500N were calculated to be 2.55 eV, 2.61 eV, and 2.5 eV, respectively. The blue shift smaller than 5 nm is observed in PL of CQD-PEG1500N below 400 nm excitation, which is probably controlled by the size and crystalline structure of the sp<sup>2</sup> carbon core and becomes more significant at longer excitation wavelength when effects from surface passivation are dominating.[3] Moreover, CQD-PEG600 shows broader PL peaks than CQD-PEG1500N, which is perhaps the effect of lower a passivation degree.

The electrochemical analysis revealed that the presence of the polymer had a reduced influence over quantum dots crystallinity, the overall electrode kinetic was a diffusion-controlled process, where LUMO electrons are extracted via an EC reaction. For CQD-PEG600 electrochemical band gap energy ( $E_{g\text{ EC}} = 2.65\text{ eV}$ ) was determined to be larger than the optical one and this difference can be explained by the exciton binding energy of conjugated polymers which is believed to be in the range of 0.4-1.0 eV. The HOMO and LUMO levels were -6.25 eV and -3.6 eV, respectively; two other reduction peaks were observed in cyclic voltamograms which can be assigned with two supplementary LUMO levels inside of bandgap at 3.9 eV and 4.35 eV.

Dark current-voltage characteristics for PEGylated nanoparticles deposited on interdigitated gold electrodes have been performed. The results showed a reproducible hysteretic behavior, which can be attributed to either mobile diffusion or to the existence of charged trapping states, due to the modification of surface chemistry.

## References

- [1] Y.P. Sun *et al.* *J. Am. Chem. Soc.* 128 (2006), 7756
- [2] L. Tang *et al.* *ACS Nano* 6 (2012), 5102
- [3] Q. Mei *et al.* *Chem. Commun.* 46 (2010), 7319.

## Figures.

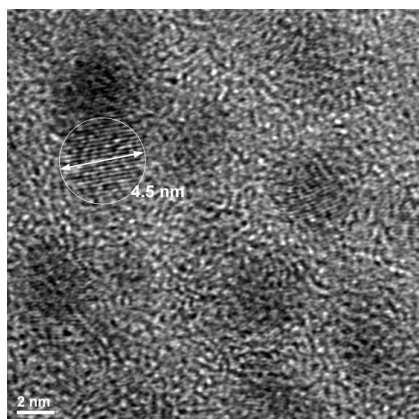


FIG 1. TEM image of carbon quantum dots after passivation with polymers reveals the dimensions and crystallinity of nanoparticles

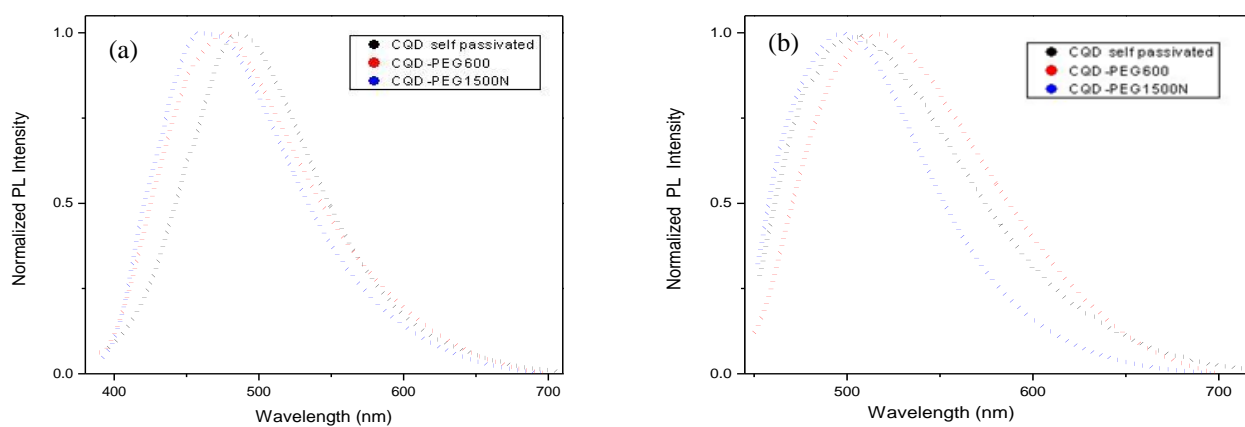


Fig 2. Photoluminescence emission spectra of surface passivated carbon quantum dots in chloroform measured at a) 380 nm and b) 440 nm excitation edge.