

# Synthesis of multicolor photoluminescent carbon quantum dots functionalized with hydrocarbons of different chain lengths

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**Abstract:** We report the synthesis of novel multicolor photoluminescent carbon quantum dots (CQDs) from multi-wall carbon nanotubes, and their covalent functionalization with amines by peptide bonds. The resulting CQDs consisted of quasi-spherical graphite nanocrystals around 10 nm diameter, which were capped by amines with different hydrocarbon chains such as propylamine, octylamine, dodecylamine and octadecylamine. The introduction of nitrogen atoms and the hydrocarbon chains in the surface of the CQDs dramatically affected their photoluminescence profiles, quantum yields and solubility. The photoluminescence emission wavelength of these novel organic-soluble CQDs depended on the excitation wavelength and their quantum yields varied with the chain length of the hydrocarbon chain attached to the surface of the carbon dots.

**Key Words:** Carbon quantum dots; Carbon nanotubes; Photoluminescence; Quantum yield.

## 1 Introduction

Amorphous carbon, graphite, and diamond were the first allotropic forms of carbon known to humanity<sup>[1]</sup>. However, the discovery of buckminsterfullerene (C<sub>60</sub>), carbon nanotubes (CNTs)<sup>[2]</sup>, and graphene in recent decades has increased researchers' interest in carbon nanostructures and has opened up exciting new fields in science and technology<sup>[1, 3]</sup>. Indeed, the scientific community has become enthusiastic about the potential applications of carbon nanostructures in energy conversion devices, biosensors, and drug delivery systems<sup>[1, 4, 5]</sup>.

Carbon quantum dots (CQDs) are a young small member of the carbon nanomaterial family<sup>[6]</sup>. CQDs first emerged in 2004 during purification of single-walled carbon nanotubes (SWCNTs) derived from arc-discharge soot by electrophoretic methods<sup>[7]</sup>. CQDs constitute a class of 'zero-dimensional structures. They usually comprise quasi-spherical graphitic nanoparticles about 10 nm<sup>[8]</sup>. The nanoparticles consist of single-, bi-, or multi-layers of sp<sup>2</sup> hybridized carbon atoms arranged in a six-membered ring, which gives rise to a graphitic core. In addition, CQDs bear some functional groups on their surfaces<sup>[3, 6, 9]</sup>.

CQDs offer unique advantages over traditional organic fluorescent agents and semiconducting quantum dots. They are cheap, chemically inert, easy to be functionalized, little toxic, and biocompatible. They display stable and tunable photoluminescence, and they can function as electron donors or acceptors<sup>[6, 10-16]</sup>.

A number of techniques are used to prepare CQDs, including laser ablation<sup>[5]</sup>, pyrolysis<sup>[8]</sup>, electrochemical synthesis<sup>[17]</sup>, supported synthesis<sup>[18]</sup>, acid oxidation<sup>[12]</sup>, microwave-assisted synthesis<sup>[19, 20]</sup>, and hydrothermal synthesis<sup>[21, 23]</sup>. The synthetic approaches are classified as either "top-down" or "bottom-up" methods, depending on the precursors. Top-down methods refer to the preparation of CQDs from large carbon materials, such as carbon fibers<sup>[24]</sup>, graphite, and CNTs<sup>[25]</sup>, whereas bottom-up methods involve the synthesis of CQDs from molecular precursors such as citric acid, glucose, and organic resins<sup>[8, 20, 21, 26]</sup>.

For several years, oxidization by mixed acids has been the standard method to break down and functionalize carbon nanomaterials<sup>[25, 27-29]</sup>. Many works have used materials such as carbon fibers, graphite, and CNTs as precursors of CQDs<sup>[17, 24, 25, 29, 30]</sup>. Recently, researchers have employed oxidization of SWCNTs,<sup>[30]</sup> multi-walled carbon nanotubes (MWCNTs), and

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graphite<sup>[25]</sup> by mixed acids to obtain CQDs with similar sizes, morphologies, and optical properties. Nitrogen-doped nanostructured carbon materials have also attracted much attention since such doping efficiently induces charge delocalization and ‘tunes’ the carbon work function<sup>[16]</sup>. CQDs post-passivated with functional amine groups (NCQDs) exhibit significantly enhanced photoluminescence as compared with the original CQDs<sup>[10]</sup>. The introduction of functional amine groups into CQDs is another effective way to modulate their emission color and efficiency<sup>[10, 16, 29]</sup>.

This study reports on a simple and reproducible route to synthesize NCQDs via MWCNT destruction. More specifically, we applied a top-down method that comprised three steps: (1) MWCNT oxidation by acid attack to obtain —C(O)OH groups; (2) treatment of the resulting product with SOCl<sub>2</sub>, to generate —C(O)Cl groups; and (3) conversion of the —C(O)Cl groups to —C(O)NR by reaction with amine. This route produced CQDs functionalized with amines via formation of peptidic bonds. We attached carbon chains with different lengths to the sp<sup>2</sup> structure of CQDs by reacting the —C(O)Cl groups with amines such as propylamine, octylamine, dodecylamine, and octadecylamine. Then the morphological and optical properties of the final CQDs were characterized.

## 2 Experimental

### 2.1 Synthesis of CQDs

MWCNTs (4.0 g, 95% purity, external diameter ranging from 10 to 40 nm, and length varying between 5 and 20 μm) were purchased from CNT Co. Ltd, Incheon, Korea, and added to a mixture of concentrated H<sub>2</sub>SO<sub>4</sub> (300 mL) and HNO<sub>3</sub> (100 mL). The resulting solution was sonicated for 2 h, which was followed by reflux at 80 ± 3 °C under constant stirring for 8 h. A light brown gas evolved.<sup>[27]</sup> After the solution was cooled and centrifuged, its pH was adjusted to 8.0 with a solution of NaOH. The product was washed four or five times with distilled water, dried in a vacuum oven at 70 °C, and identified as carboxylated MWCNTs. Reflux in excess of SOCl<sub>2</sub> (25 mL for 0.1 g) and dimethylformamide (DMF) (1 mL) at 70–72 °C for 24 h converted the carboxyl groups of the carboxylated MWCNTs to carbonyl chloride groups. The product was separated by distillation, dried in a vacuum oven at 70 °C, and identified as carbonyl chloride CQDs (CICQDs). The CICQDs were amidated by reaction with excess propylamine (PPA), octylamine (OCT), dodecylamine (DDA), or octadecylamine (ODA) in liquid phase. The products consisted of nitrogen-containing CQDs

(NCQDs) functionalized with carbon chains containing 3 (from propylamine PPA), 8 (from octylamine OCT), 12 (from dodecylamine DDA), and 18 (from octadecylamine ODA) carbon atoms. Multiple extractions with methanol (four times with 50 mL portions) separated the NCQDs from the excess amine used during the amidation reaction. 50 mL of hexane made the organic material soluble. The CQDs functionalized with amines were filtered and centrifuged at 3600 rpm for 1 h, NCQDs stay in the supernatant and the precipitate was discarded.

### 2.2 Photoluminescence quantum yield measurements

The following equation helped to calculate the photoluminescence quantum yield (*QY*) of the CQDs at an excitation wavelength of 355 nm:

$$QY_x = QY_{ST} (m_x / m_{ST}) (\eta_x^2 / \eta_{ST}^2)$$

where the subscripts ST and X denote standard and test samples, respectively, *QY*<sub>ST</sub> is the photoluminescence quantum yield of the standard, *m* refers to the gradient from the plot of integrated fluorescence intensity versus absorbance and  $\eta$  corresponds to the refractive index of the solvent. Quinine sulfate (*QY* of 54% in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution) served as a reference.<sup>[21, 31]</sup>

### 2.3 Characterization

Ultraviolet-visible (UV-vis) spectra were registered on a diode array UV-2550 Shimadzu spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a 150-W xenon lamp at room temperature. The PL decay curves were recorded by a spectrofluorimeter (Horiba-Jobin Yvon Fluorolog 3, Horiba Scientific, New Jersey, USA) using nanole of the 340 nm. Absorption and fluorescence were measured in quartz cuvettes with 10-mm optical path (Shimadzu). For this purpose, air-saturated solutions were used at room temperature. The Fourier-transform infrared (FT-IR) spectra were acquired on a Perkin Elmer spectrometer (Spectrum GX) operating in the transmission mode. 32 spectra with 2 cm<sup>-1</sup> resolution were collected. Transmission electron microscopy (TEM) was performed on a FEI Tecnai-G2-20 and JEM 2100 FEG-TEM microscope operating at 200 kV. Liquid samples were dispersed in hexane and placed on an ultrathin carbon film substrate supported by a copper grid.

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