



Fluorescence of chemically derived graphene: Effect of self-rolling up and aggregation

Xian-Fu Zhang^{a,b,*}, Suping Liu^a, Xiaona Shao^a

^a Chemistry Department, Hebei Normal University of Science and Technology, Qinhuangdao, Hebei Province 066004, China

^b MPC Technologies, Hamilton, ON, Canada L8S 3H4

ARTICLE INFO

Article history:

Received 18 May 2012

Received in revised form

24 October 2012

Accepted 6 November 2012

Available online 16 November 2012

Keywords:

Graphene

Carbon nanoscroll

Fluorescence

Aggregation

Self-rolling up

Absorption

ABSTRACT

The aggregation (inter-layer π - π interaction) and self-rolling up (intra-layer π - π interaction) of chemically derived graphene (CDG) sheets in aqueous dispersion were evidenced by spectral and TEM methods. Their effects on optical properties were studied by UV-vis-NIR absorption spectra, fluorescence emission spectra and fluorescence lifetime measurements under various CDG concentrations. At pH 8.3, CDG sheets formed carbon nanoscrolls by self-rolling up when its concentration is lower than 10 $\mu\text{g}/\text{mL}$. When the concentration is higher than that, CDG sheets aggregated. Upon aggregation, CDG exhibited the decrease of absorptivity, the change of band shape and the deviation from Lambert-Beer law due to inter-layer π - π interaction. The aggregation effect on CDG fluorescence includes the decrease of emission efficiency, the shortening of fluorescence lifetime and the relative increase of the contribution from short-lived emitting species. On the other hand, CDG self-rolling up caused the occurrence of new absorptions (500 and 960 nm) and new emission (after 500 nm), the decrease of fluorescence quantum yield and shortening of fluorescence lifetime.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The extraordinary electronic [1,2], optical [3], thermal and mechanical properties [4–10] of single-layered graphene (SLG) are all based on its unique flat 2D structure. However, the perfect flat 2D morphology of SLG could be altered by its aggregation, self-rolling up or self-folding due to various external forces. A SLG sheet is also a giant hydrophobic π - π system, which is expected to aggregate when its concentration is high, according to the cases for other aromatic molecules in poor solvents due to strong inter-layer π - π interactions [11–18]. It was found recently that carbon nanoscrolls are also a form of carbon materials [19–24] (Scheme 1). When CDG concentration is low, a single free standing SLG sheet is isolated and may self-roll up in water to be a nanoscroll to avoid contacting water molecules. This self-rolling up generally does not occur in a small aromatic molecule. It is therefore not surprising that no report is available on the study of the effect of self-rolling up on the optical properties.

Both the aggregation and self-rolling up of SLG change the π -system and therefore affect its band structure, electronic properties and hence material functionalities. Understanding the aggregation

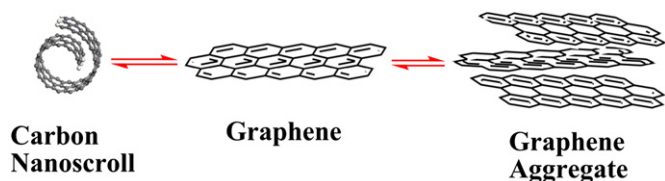
and self-rolling up of graphene and their effect on optical properties are therefore very important for fabricating and controlling properties of desired graphene materials.

Nanoscrolls are a different form of carbon nanomaterials compared to fullerenes, carbon nanotubes and graphene sheets, but their fluorescence emission and electronic absorption properties have not been reported. In contrast to this, the optical properties of fullerenes, carbon nanotubes and graphene sheets have been studied extensively.

On the aggregation behavior, there have been many studies on the small aromatic molecules and its effect on the optical properties of dyes by other researchers [13–15] and us [16,25], but no related report for graphene is available yet to the best of our knowledge. This is probably due to the solubility limitation of perfect graphene sheets in solvents. The aggregation behavior is concentration dependent and the related study needs to be carried out in solution phase, which requires graphene sheets to be soluble or dispersible. The chemical reduction of GO is a widely adopted method to produce solution dispersible graphene with large quantity [26]. Such chemically derived graphene (CDG) can be used to study the aggregation behavior. The main factors that determine the aggregation behavior of a substance are the concentration and solvent. Graphene oxide (GO) with concentrations of 0.02–0.3 mg/mL in water, for example, are existent as monolayer after exfoliation, due to its hydrophilic substituents, steric hindrance and electrostatic repulsion between sheets [27]. CDG is expected to aggregate much more aggressively due to less

* Corresponding author at: Hebei Normal University of Science and Technology, Chemistry Department, 360 Hebeidajieixidian, Qinhuangdao, Hebei Province 066004, China. Tel./fax: +86 335 838 7040.

E-mail addresses: zhangxianfu@tsinghua.org.cn, zhangxf11@hotmail.com (X.-F. Zhang).



Scheme 1. Aggregation and self-rolling up of graphene sheet.

hydrophilic substituents and less steric hindrance compared to GO.

An aggregate containing n SLG sheets in a solvent may not have the same steric structure as that of n -layered graphene in solid state, due to the dynamic aggregation equilibrium in solvents. For example, a SLG dimer in aqueous phase is very likely different from a typical double-layered graphene sheet, since the former can be formed randomly by partially overlapping of two SLG sheets with undefined distance and orientation, while the latter is closely packed by two parallel SLG sheets with a distance of 0.34 nm.

Based on above considerations, we measure the electronic absorption and fluorescence properties of CDG under different concentrations to reveal its aggregation and self-rolling up effect at high and low concentrations, respectively, based on our previous experience with graphene [28–30]. In contrast a few reported studies on the fluorescence of graphene in solution did not take these factors into consideration [31–35].

2. Materials

The synthesis and characterization of graphene oxide (GO) and CDG were already described by us previously [29,30,36]. Double distilled deionized water was further purified by Millipore Milli-Q system. All other reagents are analytical grade and commercially available.

For all absorption and fluorescence measurements, 0.1 mg/mL [CDG] was used as the stock solution, which was diluted to get the desired concentrations. Excessive ammonium in CDG stock solutions was evaporated at 50 °C in water bath to allow pH ca. 8.3. The pH value was adjusted by 1 mol/L aqueous HCl solution when necessary. Controlled experiments in the absence of CDG were examined and no fluorescence was found.

3. Experimental

UV–vis–NIR absorption measurements were made with a StellarNet BLACK Comet C-SR diode array miniature spectrophotometer connected to deuterium and halogen lamp by optical fiber in 10 mm quartz cuvettes. Fluorescence spectra and lifetimes were monitored using Edinburgh Instruments FLS 920, with 5 and 1 nm slits, respectively.

All measurements were carried out at room temperature of 22 ± 2 °C. All fluorescence spectra were corrected for the sensitivity of the photo-multiplier tube. The fluorescence quantum yield (Φ_f) was calculated by $\Phi_f = F_s A_0 / (F_0 A_s)$, in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, the subscript 0 stands for a reference compound and s represents samples. All solutions were air saturated. Fluorescence lifetime was measured by time-correlated single photon counting method with excitation at 379 nm by a CdS portable diode laser (50 ps pulse width) and emission was monitored typically at 460 nm. Fluorescence lifetimes were obtained by fitting the experimental data to $I(t) = A + \sum A_i \exp(-t/\tau_{fi})$ by deconvolution method.

4. Results and discussion

4.1. Graphene characterization

The preparation and characterization of CDG have also been described in our previous report [28–30]. The pH value of 8.3 was

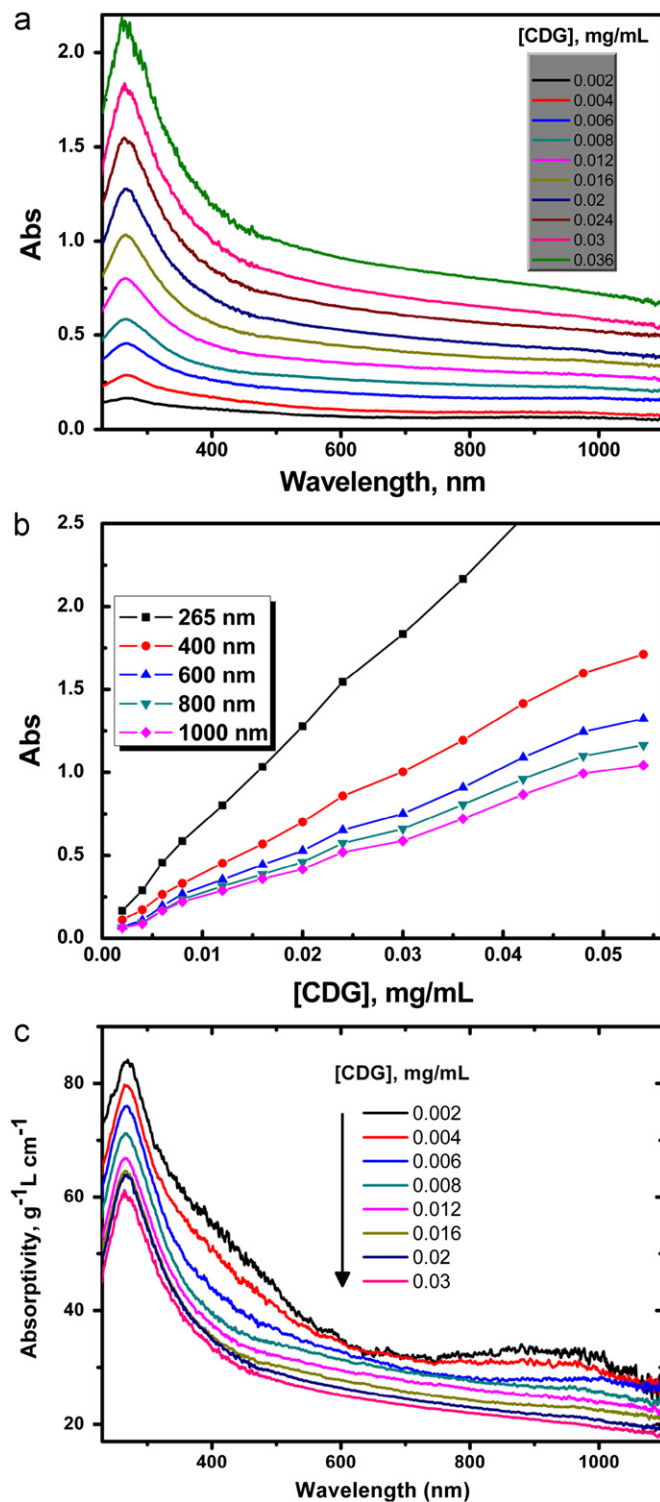


Fig. 1. The dependence of UV–vis–NIR absorption spectra of CDG on its concentration (a), the plot of absorbance against [CDG] (b) and the plot of absorptivity upon CDG concentration (c). Solvent: water, pH 8.3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/5400945>

Download Persian Version:

<https://daneshyari.com/article/5400945>

[Daneshyari.com](https://daneshyari.com)