Sensors & Transducers, Vol. 225, Issue 9, September 2018, pp. 36-40

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Sensors & Transducers

Published by IFSA Publishing, S. L., 2018
http://www.sensorsportal.com

Photoluminescence of Graphene Oxide and Graphene Quantum Dots

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Received: 25 June 2018 /Accepted: 31 August 2018 /Published: 30 September 2018

Abstract: Graphene oxide (GO) and Graphene Quantum Dots (GQDs) have several properties for different applications. The photoluminescence properties are essential to understand the behavior of materials. In this study, we studied the dispersion of GO and GQDs in different solvents and we had measured the UV-Vis absorption and photoluminescence (PL) spectra for GO and GQDs. In addition, we had monitored their spectra at different values of pH.

Keywords: Photoluminescence, Graphene Oxide, Graphene Quantum Dots, DMSO, DMF, Acetonitrile.

1. Introduction

Carbon is seemingly the most interesting component in the periodic table. Also, it is widely used in industry for manufacturing materials. The fundamental feature of carbon is the unique ability for combining with other elements. Carbon exist in various allotropic forms such as, fullerene (0D), Carbon nanotubes (CNTs), one-dimensional (1D) and along cylindrical in shape. (1D). The most widely recognized type of carbon is graphite [1-3]. It is a three-dimensional (3D) carbon material and in 2004, came a surprise to the physics community when Geim, Novoselov and their collaborators first isolated single layer sample from graphite [3]. Graphene is two-dimensional (2D) materials, consisting of a single layer of carbon atoms in honeycomb lattice, as characterized by (sp^2) bonding. However, graphene is a zero-band gap semiconductor. Graphene has gotten much attention in the scientific community due to many properties and different application. [3-4]. There are many methods for fabrication of graphite; such as chemical vapour deposition (CVD), and micromechanical exfoliation of graphite [5].

One of functionalized product is graphene oxide. It has different properties when compared to graphene. GO is heavily oxygenated with functional groups on the basal plane or at the edge. Because the functional groups, GO becomes hydrophilic (have a strong affinity for water) which allows better interaction with polar solvent. Also, GO contains a complex of sp^2 and sp^3 hybridized carbon atoms covalently bonded [6].

Graphene Quantum Dots (GQDs) is a nano-crystal a novel material of graphene. The difference between graphene and GQDs is the modification of electron behavior because of quantum confinement.

2. Structures of GO and GQDs

Graphene consists on a monoatomic layer made of carbon atoms stacked densely in hexagonal lattice. Graphene is a zero-gap material with one type of electron and one type of hole. Each carbon of graphene its (sp^2) hybridization between (s), (P_x) and (P_y) orbitals, thus makes a strong (covalent) bond (σ-bond) with neighboring carbon atoms, giving rise to (C – C – C) bond with an angles of 120°. The length is 0.142 nm for strong bonds with an inter-planar distance of approximately 0.335 nm. The remaining (Pz) orbitals on each carbon overlap with their three neighboring carbons to form a band of filled (π) bonding orbitals. But, there is an empty (π*) anti-bonding called the conduction band. Thus, the planner carbon structure as well as the delocalized the (π) electrons through the plane, helps for various applications [3-4].

Graphene Oxide (GO) is layer of graphene with oxygen functional group such as hydroxyl (OH), carbonyl (C=O) and alkoxy (C–O–C) groups. Graphene oxide is a hybrid of carbon atoms; it is consisting a mixture of sp^2 and sp^3 bonded carbon. GO is an electronically hybrid material that features both conducting π-states from sp^2 carbon sites and a large energy gap (carrier transport gap) between the σ-states of its sp^3-bonded carbons. The tunability of the ratio of the sp^2 and sp^3 fractions by reduction chemistry is a powerful way to tune its bandgap and therefore controllably transform GO from an insulator to a semiconductor and to a graphene-like semi-metal [7].

GO sheets have a thickness of ~1 nm, which is a larger than graphene, due to the presence of oxygen and functional groups above and below the carbon basal plane. This structure for graphene oxide can been observed in the matrix of the sp^2 carbon and sp^3 (C-O) by Raman spectroscopy, transmission electron microscopy and FTIR [7].

However, GQDs its consist of carbon and hydrogen with functional group such as (OH, CO and COOH). The dimensions for GQDs is less than (100 nm). There is different size and thickness of GQDs that affect the electrical and optical properties.

Here we report the photoluminescence (PL) for GO and GQDs in various solvents. We measured absorption and photoluminescence spectra at different values of pH for GO and GQDs [8].

3. Experimental

The spectral (UV-Vis) absorption and Photoluminescence (PL) characteristic of GO in various solvents such as Distilled Water, Acetonitrile, Dimethyl Sulfoxide (DMSO), N, N Dimethylformamide (DMF), Acetone, Ethanol, Methanol, in the same concentration were studied. The GO did not go in the solution immediately. So, the dispersions were sonicated in an ultrasound for (1 h) to remove the large lumps. The optical properties for all samples were investigated within wavelength region from 200 to 600 nm by using UV-Vis spectrometer (Biochrom libra S80PC) and PL by (Shimadzo RF-5301PC). GO showed very good dispersion in Distilled Water, Acetonitrile, DMSO, DMF and give a good photoluminescence [9-10]. Fig. 1, shows the absorption spectrum of GO dispersion in distilled water. The absorption peak of GO was seen at 231 nm, and a weak shoulder peak at the 303 nm. The first peak is attributed to $\pi - \pi^*$ transition of C-C bonds, while the second peak is coming from $n - \pi^*$ transition of C=O bond in sp^3 hybrid regions [6, 11]. This result is similar with the work reported by Khan, *et al*. (2015).

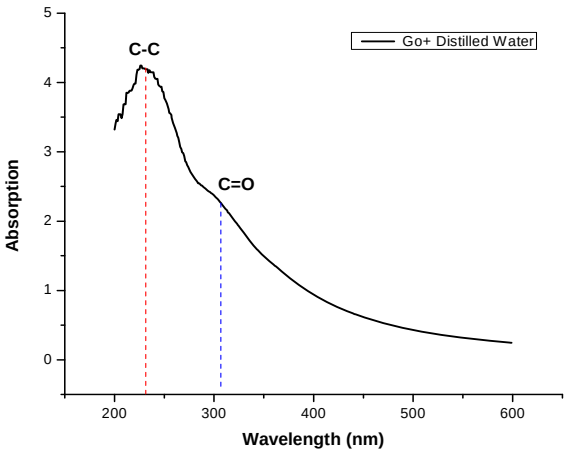

Fig. 1. UV-vis absorption spectra of GO aqueous solutions.

Furthermore, the spectra of GO in Acetonitrile, DMSO and DMF have peak at 230 nm and the shoulder at 300 nm absorption. As shown in Fig. 2 [9-10].

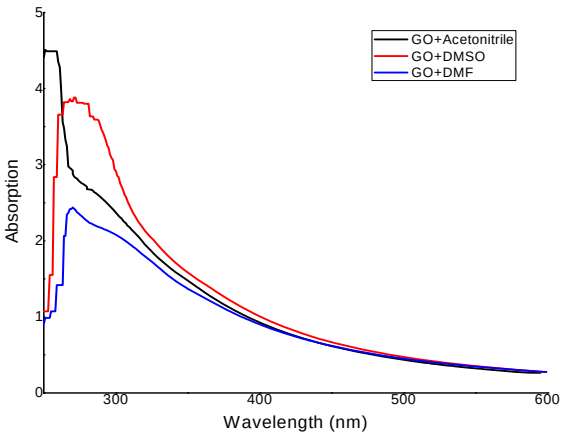

Fig. 2. UV-Vis absorption spectra of GO in different solvent.

The photoluminescence emission spectra for excitation wavelength from 275 to 400 nm, were obtained. The broad emission band appears at 400 to

600 nm (shown in Fig. 3). It can be seen that there are three bands one at 430 nm, next at 470 nm and third at 540 nm [11]. These bands are in agreement to the literature reports by Shang, *et al*. (2012).

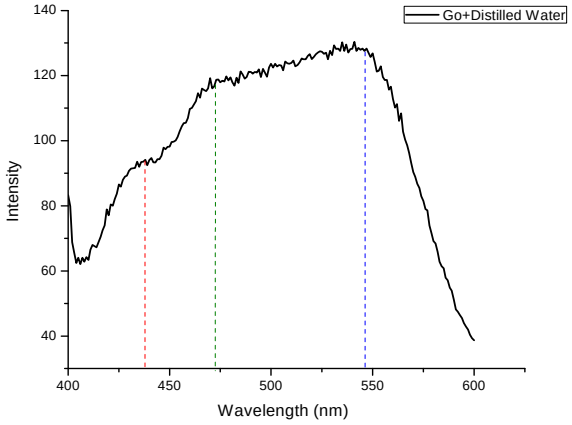

Fig. 3. PL spectra for GO aqueous solutions.

The photoluminescence quantum yield was measured by using the following equation [12].

$$QY = \frac{\text{Number of Photons Emitting}}{\text{Number of Photons absorption}} \quad (1)$$

For Photoluminescence quantum yield measurements were done with a standard of known quantum yield value.

$$QY_{GO} = QY_s \times \frac{\int F_{GO}}{\int F_s} \times \frac{A_s}{A_{GO}} \times \frac{n_{GO}^2}{n_s^2}, \quad (2)$$

where QY is the quantum yield, F is the measured integrated emission intensity, A optical density and n is the refractive index [12]. The subscript "s" refers to the reference fluorophore coumarin 1 of known quantum yield. the photoluminescence yield of GO in Distilled water was found lower than 1 % [7]. Also, GO showed very good dispersion in Acetonitrile, DMSO and DMF. All these solvents showed significant dispersion duo to polarity of solvents. We observed the absorption peaks of GO in Acetonitrile, DMF and DMSO are similar to that in distilled water [9-10].

However, the effect is different in ethanol, methanol and acetone where the PL gets quenched due to relaxation without emission of a photon. That is because ethanol, methanol and acetone are mildly polar solvents so the interaction with hydrophilic GO is reduced as shown in Fig. 4. In fact, GO forms insoluble miscelle in ethanol, methanol and acetone [9-10].

In addition, we notice GO aqueous solutions is acidic (pH = 4.5). The spectra of GO have strong pH dependence. The pH was increased from strongly acidic to strong basic [13]. Excitation and emission spectra were measured for different values of pH (1.7, 2.5, 3.78, 5.6,7.2, 9.1 and 10.25) by adding drops of dilute HCl or NaOH. The absorption spectra have the same peak at 280 and 305 nm independent of pH. But PL dramatically changed in intensity and shape. This shows that GO undergoes protonation only in the excited state [13]. That mean all the PL shown below are for the GO exciplex. When the pH is recorded from 7 to 3 the peak at 550 nm gets enhanced in intensity. That means GO is inherently acidic in nature (shown in Fig. 5).

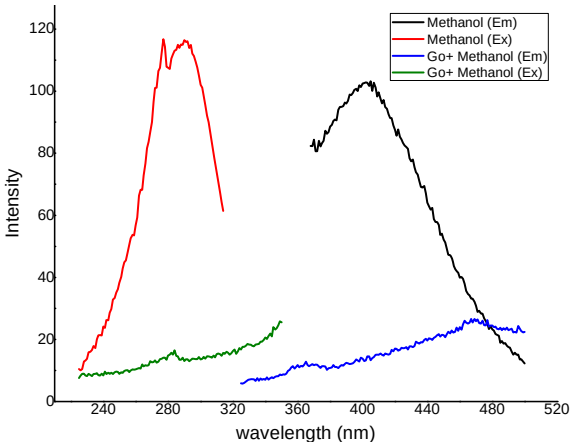

Fig. 4. PL emission spectra for GO in methanol.

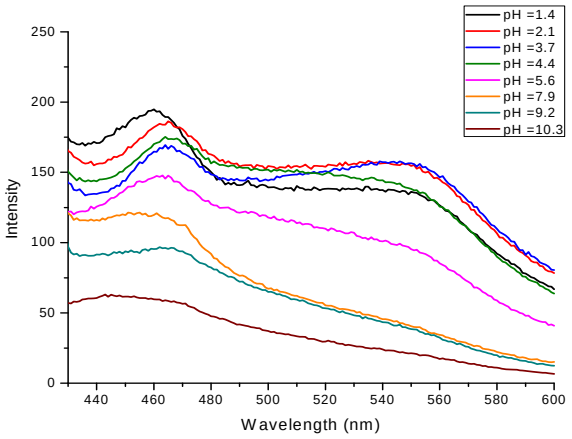

Fig. 5. PL spectra for GO aqueous solutions for different values for pH.

GQDs is the most popular because the efficient fluorescent nanocarbons and the PL stability. The intensity of the GQDs depend on the size. GQD are readily soluble in water and many polar organic solvents. Fig. 6, shows the absorption spectrum of GQDs have peak at (270 nm). This comes from the $\pi - \pi^*$ transition of C=C bounds according to previous report. Also, the shoulder peak at (290 nm) from $n - \pi^*$ transition of C=O.

Photoluminescence spectra of GQDs showed in Fig. 7. We observed the peak wavelength at ($\sim$ 420) nm only irrespective of wavelength of excitation. The intensities change as the wavelength of the excitation change.

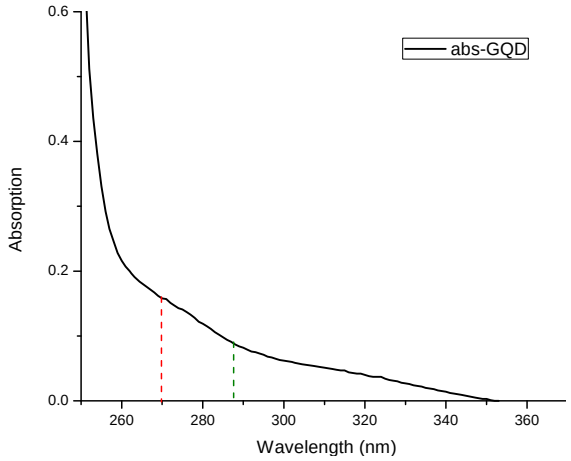

Fig. 6. UV-Vis absorption spectra of GQDs in distilled water.

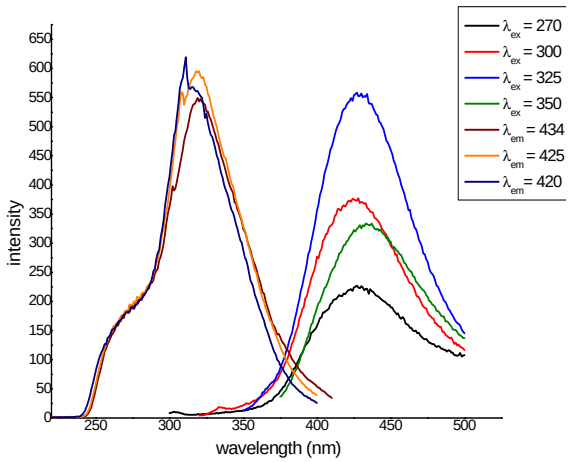

Fig. 7. PL emission spectra for GQDs in distilled water.

Fig. 8, shows 2 ml of GQDs in 1 ml of different solvents such as acetonitrile, ethanol and DMSO. And we found PL spectral features of QDs are not dependent on solvents.

As shown Fig. 9 and Fig. 10 photoluminescence of GQDs does not depend upon pH of water, since the peak wavelength and intensity are the same for pH 3.2 to 10.5.

4. Conclusion

We have studied GO in different solvents. We showed GO is very stable in distilled water, acetonitrile, DMF and DMSO. The absorption peak of GO was seen at 231 nm, and a weak shoulder peak at the 303 nm. Also, the UV-Vis spectra of GQDs in different solvents showed two shoulders. In addition, we compared the photoluminescence of GO and GQDs and we noticed the intensity of GO depended on the solvents. However, the spectra of GQDs does not depend upon the solvents. GO has strong pH dependent visible photoluminescence from aqueous dispersion. The wavelength emission in basic conditions appear near 470 nm but in acidic conditions appear at 540 nm. This is a clear evidence for exciplex formation for GO. In contrast, the peak wavelength and intensity are the same for different pH in photoluminescence of GQDs.

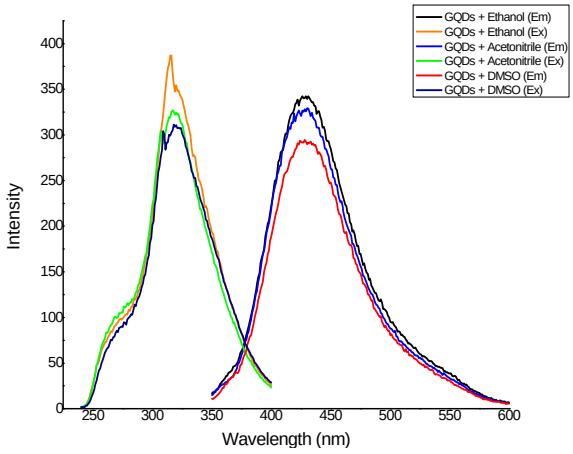

Fig. 8. PL emission spectra for GQDs in different solvents.

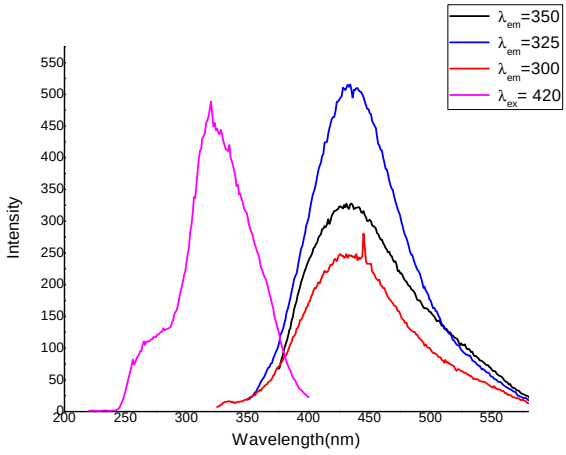

Fig. 9. PL spectra for GO aqueous solutions for pH = 3.2.

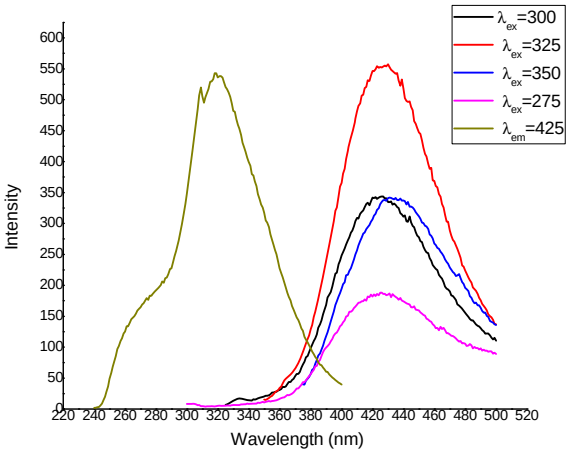

Fig. 10. PL spectra for GO aqueous solutions for pH = 10.5.

Acknowledgment

We thank King Abdulaziz City for Science and Technology (KACST) (1-17-01-001-0075) for the financial support in this research work.

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