

Fluorescence Quenching as an Efficient Tool for Sensing Application: Study on the Fluorescence Quenching of Naphthalimide Dye by Graphene Oxide

Sanaz Seraj, Shohre Rouhani

Abstract—Recently, graphene has gained much attention because of its unique optical, mechanical, electrical, and thermal properties. Graphene has been used as a key material in the technological applications in various areas such as sensors, drug delivery, super capacitors, transparent conductor, and solar cell. It has a superior quenching efficiency for various fluorophores. Based on these unique properties, the optical sensors with graphene materials as the energy acceptors have demonstrated great success in recent years. During quenching, the emission of a fluorophore is perturbed by a quencher which can be a substrate or biomolecule, and due to this phenomenon, fluorophore-quencher has been used for selective detection of target molecules. Among fluorescence dyes, 1,8-naphthalimide is well known for its typical intramolecular charge transfer (ICT) and photo-induced charge transfer (PET) fluorophore, strong absorption and emission in the visible region, high photo stability, and large Stokes shift. Derivatives of 1,8-naphthalimides have found applications in some areas, especially fluorescence sensors. Herein, the fluorescence quenching of graphene oxide has been carried out on a naphthalimide dye as a fluorescent probe model. The quenching ability of graphene oxide on naphthalimide dye was studied by UV-VIS and fluorescence spectroscopy. This study showed that graphene is an efficient quencher for fluorescent dyes. Therefore, it can be used as a suitable candidate sensing platform. To the best of our knowledge, studies on the quenching and absorption of naphthalimide dyes by graphene oxide are rare.

Keywords—Fluorescence, graphene oxide, naphthalimide dye, quenching.

I. INTRODUCTION

GRAPHENE is a single layer of graphite with one atom thickness. Since its discovery in 2004 [1]-[6], it has become one of the important materials in the field of sensors, drug delivery, super capacitors, and solar cell. Graphene oxide (GO) contains many functional groups including carboxylic, epoxy, and hydroxyl groups [7], [8]. These functional groups provide it a superior quencher that can strongly interact with a variety of fluorophores [9]-[13]. Naphthalimide dye is a well-known dye with strong absorption and emission in the visible region, high photostability which can be used in optical sensors [14]-[22]. In this study, the absorption of naphthalimide dye by GO was studied by UV-Vis

spectroscopy, and quenching property of GO on the fluorescence intensity of naphthalimide dye in an aqueous solution was evaluated.

II. EXPERIMENTAL

A. Materials

GOs were purchased from Nano SANY Co. The product number of GO is US 7906, CAS 7732-18-5. 4-(2-aminoethylene) amino-N-allyl-1,8-naphthalimide(N) was synthesized and characterized in our laboratory. A 5×10^{-5} M stock solution of dye was used in spectroscopic investigations.

B. Equipment

All fluorescence measurements were performed using a Perkin-Elmer LS55 fluorescence spectrophotometer. UV-VIS absorption spectra were collected on a CECIL-CE9200 spectrophotometer. Atomic force microscope (AFM) was recorded on an operating in tapping mode.

III. RESULTS AND DISCUSSION

A. Characterization of GO

To characterize the used commercial GO, UV-vis absorption and SEM techniques were applied. UV-vis absorption spectrum of GO aqueous dispersion (30 mg/l) showed a maximum absorption at 229 nm due to the π - π^* transition of aromatic C=C bonds. SEM technique investigated planar morphology of GO.

B. Atomic Force Microscopy Image

AFM technique was used to measure the thickness of the GO flakes. Whereas the height of unmodified GO was 2.6 nm, that of GO stacked with naphthalimide dye grows to 6.5 nm. The latter indicates adsorption of dye on GO sheets (Fig. 2).

C. Absorption Characteristics of N/GO

To investigate the interaction between the naphthalimide dye and GO, the absorption peak of dye in the presence of various concentration of GO was obtained (Fig. 3). As shown in Fig. 3, naphthalimide dye exhibits characteristic absorption peaks at about 302 and 450 nm. By the addition of different concentrations of GO, the intensities of maximum absorption spectra in 302 nm increase. The peak at 450 nm for (1×10^{-5} M) is too weak. The increase in the intensities of UV absorption spectra with the GO concentration was only due to the increasing intensity of GO absorption. To verify the quenching

Sanaz Seraj is with the Department of Organic Colorants, Institute for Color Science and Technology, Tehran, Iran (phone:+989128206380, e-mail:sanazseraj10@gmail.com).

Shohre Rouhani is with the Department of Organic Colorants, Institute for Color Science and Technology, Center of excellence for Color Science and Technology(CECST), Institute for Color Science and Technology, Tehran, Iran (e-mail: rouhani@icrc.ac.ir).

mechanism, the shape and shifts of absorption peaks of UV-Vis spectrum were investigated. The UV-Vis absorption spectrum of the fluorophore would change during the static quenching due to the formation of a complex between the ground state of the fluorophore and the quencher, while no

absorption spectrum change should be observed in the dynamic quenching [23]. No new band was observed in the UV-Vis absorption spectra of naphthalimide in the presence of various concentrations of GO. This spectrum indicates that the quenching was followed by a dynamic quenching process.

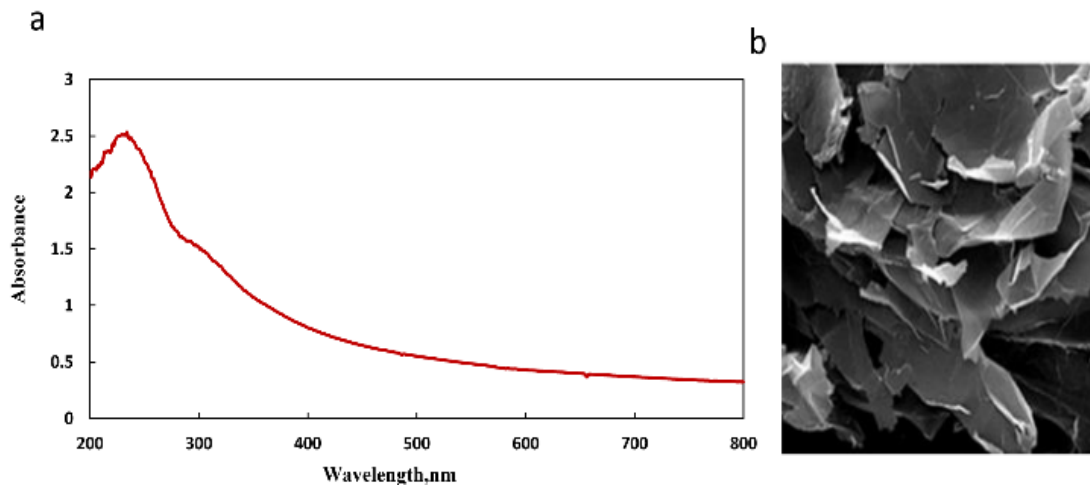


Fig. 1 (a) UV-Vis absorption spectrum of 15 µg/mL GO aqueous dispersion (b) SEM of used GO

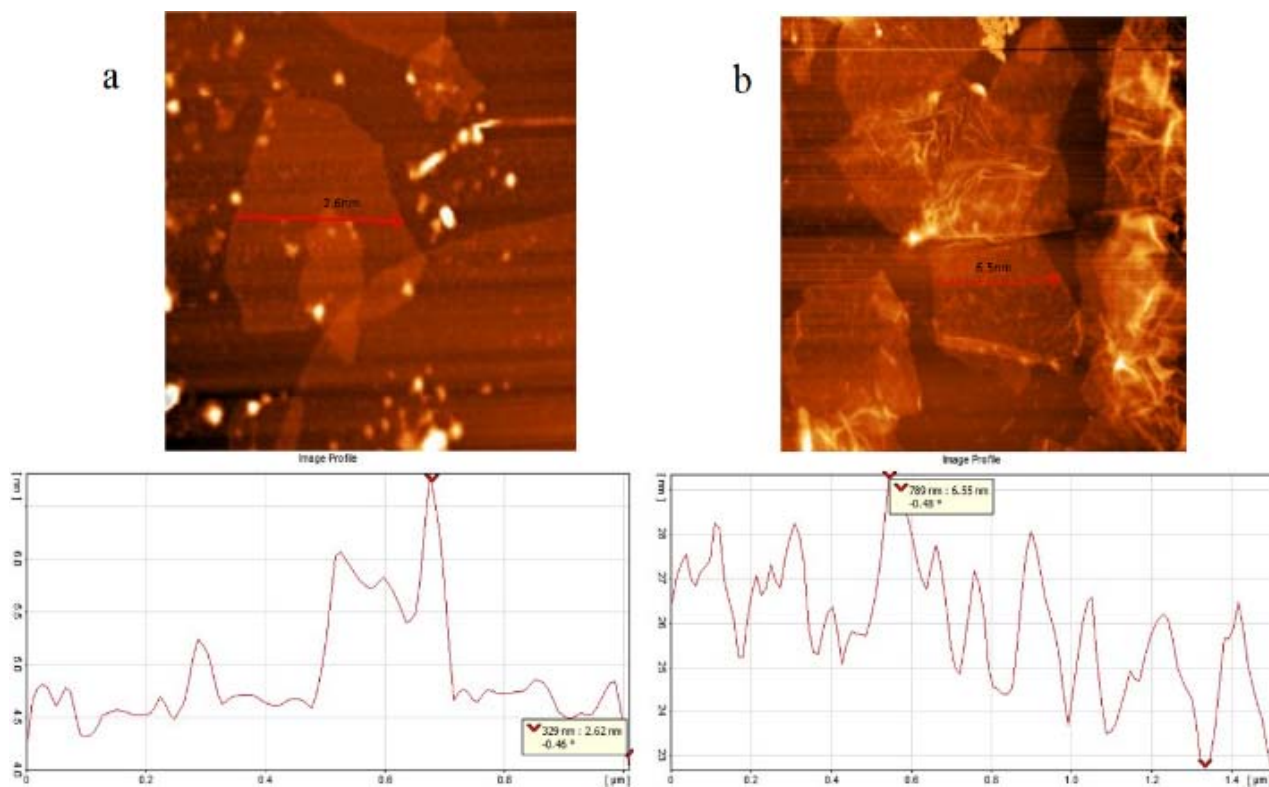


Fig. 2 AFM images of (a) GO, (b) naphthalimide dye/GO

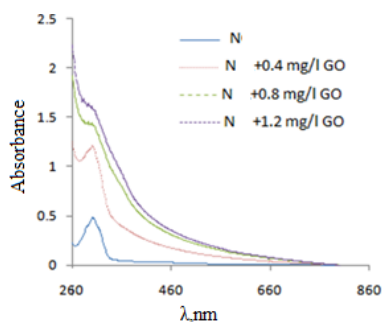


Fig. 3 UV-Vis absorption spectra of N aqueous solution in the absence and presence of GO

D. Fluorescence Studies

As shown in Fig. 4 (a), the fluorescence emission intensity of naphthalimide dye gradually decreased with increasing GO

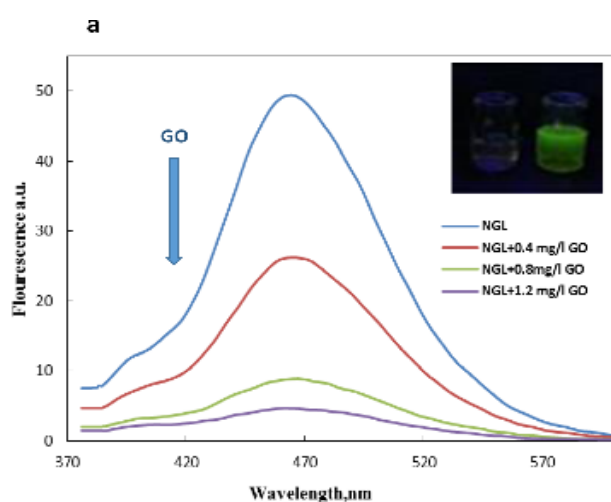


Fig. 4 (a) Fluorescence quenching spectra of 1.0×10^{-5} M N in the presence of various concentration of GO, (b) Red shift emission of N spectra in the presence of GO

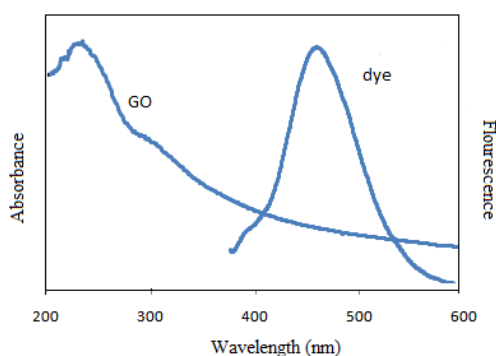
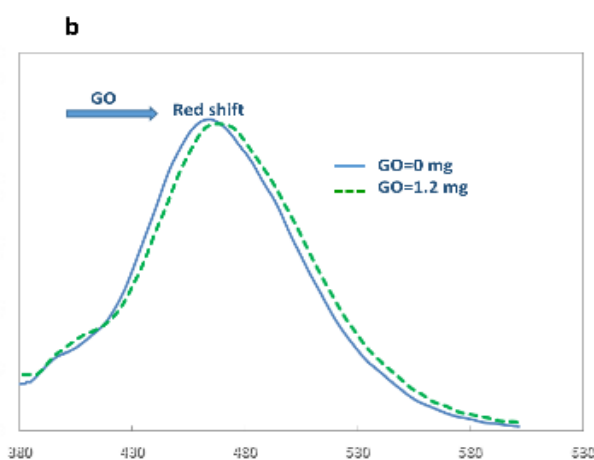


Fig. 5 UV-Vis absorption spectra of GO aqueous solution and fluorescence emission of N

The quenching of naphthalimide dyes could take place by several possible processes such as energy transfer or electron transfer. Since the absorption spectra of graphene did not overlap with the fluorescence emission spectra of naphthalimide dye (Fig. 5), energy transfer between N and GO

concentration. It shows that GO is indeed an efficient quencher of the naphthalimide fluorophore. In addition, GO did not have any fluorescence at the same excitation wavelength of naphthalimide approved that the observed quenching was due to the interaction between dye and GO and not an inner filter effect or reabsorption. As can be seen in Fig. 4 (b), an apparent red shift of (6 nm) takes place in the maximum emission peak as GO concentration grows from 0 to 1.2 mg/l. It seems that the naphthalimide dye strongly adsorbed on the GO surface via π - π interactions. In spite of the fact, GO was the oxidized form of graphene with carboxylic acid group at the edge and hydroxyl and epoxy groups on the basal plane and aromatic areas with sp^2 carbons [24], [25]. Therefore, GO could have π - π stacking interaction with aromatic rings of naphthalimide dye.

was not probable here. So, it seems that the fluorescence quenching of naphthalimide dye with graphene follows an electron transfer process. The same behavior for GO and coumarine dye was reported previously [26].

IV. CONCLUSION

In conclusion, GO was found to strongly interact with naphthalimide dye (N) by fluorescence quenching. The interaction between naphthalimide dye and GO was studied by UV-Vis and fluorescence spectroscopic techniques. The results indicated that graphene is a very efficient quencher for naphthalimide molecule. These experimental and theoretical results are of potential importance in understanding the mechanism of interaction between graphene and naphthalimide dye and would be a useful guide for efficient fabrication of graphene-based sensors.

ACKNOWLEDGMENT

We would like to thank the Center of Excellence for Color

Science and Technology (CECST), Institute for Color Science and Technology, Tehran-Iran for providing us a good environment and facilities to complete this project.

REFERENCES

- [1] C. H. Jianrong, M. Yuqing, "Recent Advances in Nanotechnology Applied to Biosensors", *Nanotechnology and biosensors*. Biotech. Adv 22,505-518,2009.
- [2] S. Kumar, A. G. Venkatesh, "Nanotechnology based biosensors and diagnostics: Technology push versus industrial/healthcare requirements", *Bio Nano Sci.*, 2, 115-126. 2012.
- [3] A. K. Geim, K. S. Novoselov, "The rise of graphene", *Nat Mater.*, 6, 183-191, 2004.
- [4] C. H. Lu, H. Yang, "A graphene platform for sensing biomolecules", *Angew. Chem.*, 48, 4785-97, 2009.
- [5] E. Narvaez, A. Merkoci, "Graphene oxide as an optical biosensing platform", *Adv. Funct. Matter.*, 24, 3298-3308, 2012.
- [6] H. Chang, L. Tang, "Graphene fluorescent resonance energy transfer aptasensor for thrombin detection", *Anal. Chem.*, 82, 2341-2346, 2011.
- [7] L. Sheng, J. Ren, "PVP coated graphene oxide for selective determination of ochtotoxin A via quenching fluorescence of free aptamer", *Biosens Bioelectron*, 26, 3494-3499, 2011.
- [8] Y Hu, F Li, "Biocompatible graphene for bioanalytical application", *Angew. Chem*, 50, 6851-6858, 2009.
- [9] X. Wang, K. Qu, "Ultrasensitive and selective detection of a prognostic indicator in early stage cancer using graphene oxide and carbon nanotube", *Adv. Funct. Matter*, 20, 3967-3971, 2010.
- [10] S. He, B. Song, "Graphene nanoprobe for rapid, sensitive and multicolor fluorescent DNA analysis", *Adv. Funct. Matter*, 20,453-460,2009.
- [11] Y. Zhau, X. Gang, "Review on the graphene based optical fiber chemical and biological sensor", *Sens Actuators B Chem*, 231,324-340,2016.
- [12] X. Zhu, Y. Shen, "Detection of microRNA by using reduced graphene oxide", *Chem. Commun*,51,10002-10005,2014.
- [13] Z. H. Li, M. He, "Graphene materials based energy acceptor systems and sensors", *J Photochem Photobiol B*,18,1-17,2014.
- [14] J. Kim, L. J. Cote, "Visualizing graphene based sheets by fluorescence quenching microscopy", *J. Chem. Phys.*, 132,260-267,2010.
- [15] M. Hurtado, M. Ortiz, "Efficient fluorescence quenching in electrochemically exfoliated graphene decorated with gold nanoparticles", *C. Acuna, Nanotech*,27,2010.
- [16] A. Kasry, A. Ardakani, S. Tulevski, M. Copel, "Highly Efficient Fluorescence Quenching with Graphene", *J. Phys. Chem*, 116, 2858-2862, 2012.
- [17] R. S. Swathi, K. L. Sebastian, "Resonance energy transfer from a dye molecule to graphene", *J. Chem. Phys*,130, 054703-09,2008.
- [18] R. S. Swathi, K. L. Sebastian, "Long range resonance energy transfer from a dye molecule to graphene has (distance) (-4) dependence. *J. Chem*", *Phys*, 130,0861011-0861013,2009.
- [19] A. Airinet, R. Tigolanu, E. Rusu, D. Dorohoi, "Fluorescence Quenching of Anthracene by Nitroaromatic Compounds", *Dig J Nanomater Bios*, 6,1265-1272,2009.
- [20] J. R. Lakowicz, "Topics in Fluorescence Spectroscopy", 2nd ed., Kluwer Academic/Plenum Publishers, New York/London/Moscow/Dordrecht, 2002 (Chapter 2).
- [21] F. Galindo, M. I. Burguete, R. Gavara, S. V. Luis, *J. Photochem. Photobiol. A: Chem.* 178,57-61,2006.
- [22] X. Qian, Y. Xiao, *Chem. Commun.*,46,6418-6436,2010.
- [23] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*. Kluwer Academic/Plenum Publishers, New York,1999.
- [24] A. Lerf, H. Forster, M. Klinowski, "Structure of Graphite Oxide Revisited". *J. Phys. Chem.*, 102,4477-4482,1998.
- [25] J. Peredes, S. Villar, "Graphene Oxide Dispersions in Organic Solvents" *J. Langmuir*,24,10560-10564,2008.
- [26] M. Ghazinejad, H. Hosseini, H. Reiber, J. Kyle, "Fluorescence Quenching Metrology of Graphene. Photonic and Phononic Properties of Engineered Nanostructures", 8994, 277-285, 2015.