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

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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-aminoethylenene) amino-N-allyl-1,8-naphthalimide(N) was synthesized and characterized in our laboratory. A $5 \times 10^{-5}$ 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 $\pi-\pi^*$ 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 NGO

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 characteristics 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 ($1 \times 10^{-5}$ M) is too week. 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...
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
**D. Fluorescence Studies**

As shown in Fig. 4 (a), the fluorescence emission intensity of naphthalimide dye gradually decreased with increasing 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 sp² carbons [24], [25]. Therefore, GO could have π-π stacking interaction with aromatic rings of naphthalimide dye.

**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.

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REFERENCES


