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Effect of pH on fluorescence quenching of organic dyes by graphene oxide

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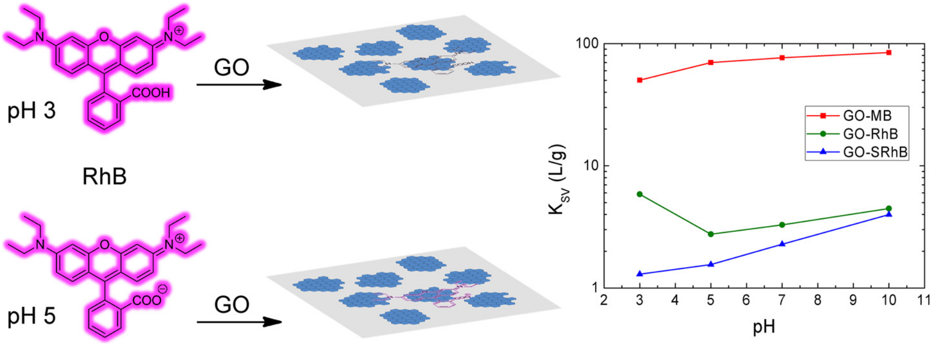
GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide (GO) has been recently used in several fluorescence sensing systems as a fluorescence quencher. The interactions between GO sheet and fluorophore directly affect the fluorescence quenching efficiency of GO. To understand these interactions, methylene blue (MB), rhodamine B (RhB) and sulforhodamine B (SRhB) were used as model fluorophores at various pH values in aqueous buffer solutions. The synthesized GO was characterized by UV–vis spectroscopy, infrared spectroscopy, thermogravimetric analysis, zeta potential measurement and particle size measurement. The interactions between GO and dyes were studied by fluorescence spectroscopy. The fluorescence quenching efficiency of GO to each dye is differently affected by the pH attributed to electrostatic interaction, π–π stacking and hydrogen bonding. While electrostatic interaction is the most important interaction for GO–MB and GO–RhB, the π–π stacking also plays an important role for GO–SRhB system. The temperature dependence of the quenching efficiency suggests a static quenching mechanism and the decrease of the quenching efficiency with the reducing GO size is probably due to a lower number of sp^2 domains in the GO sheets.

1. Introduction

Graphene oxide (GO) is a carbon-based nanomaterial produced by treating graphene with a concentrated acid and a strong oxidizing agent. As a result, some of the sp^2-hybridized carbons are functionalized with oxygen-containing functional groups, including hydroxyl, epoxide and carboxyl groups [1,2]. Despite being first synthesized in the 1850s [3], it was not until the past decade that GO has truly drawn

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great attention from scientific community when it was found to be the promising precursor for large scale production of solution-processable chemically converted graphene (CCG), which is also known as reduced graphene oxide (rGO) [4–7]. Moreover, GO and its derivatives have since then demonstrated a myriad of applications, including drug delivery [8–10], catalysis [11–14], photodegradation [15–18], wastewater treatment [19–24], water desalination [25,26], antibacterial composite production [27,28] and chemical sensor fabrication [29–38].

Numerous studies have revealed that GO, as well as graphene, can effectively quench the fluorescence signal of various fluorophores [32–42]. The fluorescence quenching mechanisms of GO have been proposed to be associated with Förster resonance energy transfer (FRET) [37,38] or photoinduced electron transfer (PET) [40,41]. This unique ability makes detection of metal ions [32,33], drug molecules [34], biomolecules [35–37] and nucleotides [38] viable. Basically, when GO and fluorophore are close to each other, the energy or excited electron will transfer from fluorophore to GO and thus the fluorescence signal is quenched. In the presence of an appropriate analyte, however, the fluorophore is separated from the surface of GO by a stronger interaction, hence the fluorescence signal is recovered.

Obviously, the interaction between GO and fluorophore is an important factor affecting the efficiency of the aforementioned sensing system. If the attractive interaction is too strong, GO and fluorophore will bind tightly together such that the analyte cannot separate the fluorophore from the GO. Therefore, the system does not respond to the analyte. On the other hand, if the interaction is too weak, GO might not be able to effectively quench the fluorescence signal, so the sensitivity of the system is low. Consequently, the study of parameters or conditions affecting the interactions between fluorophore and GO and the fluorescence quenching efficiency of the system are beneficial for designing effective GO-based sensing systems.

An early study reported that GO surface is negatively charged and it can quench the fluorescence of cationic methylene blue dye more efficiently than that of the anionic eosin dye, due to the electrostatic interaction [39]. Recently, a study on the adsorption capacity toward methylene blue of graphite oxide, an undispersed solid form of graphene oxide, with different oxidation levels suggested that highly oxidized graphite oxide has superior adsorption capacity than graphite oxide with lower oxidation degree because of more negatively-charged surface of the former, strengthening the electrostatic interaction [43]. Additionally, evidences for the existence of π–π stacking and hydrogen bond between GO and other molecules were also reported [8,44]. Since GO–dye systems are related to various applications, they are mostly utilized at different environments. Therefore, it is essential to understand how environmental conditions such as pH variate intermolecular interactions between GO and dyes and affect the fluorescence quenching. However, the study of pH effects on fluorescence quenching by GO has not been thoroughly investigated for different electrostatically charged dyes. To understand the role of intermolecular interactions in the fluorescence quenching efficiency of GO, we therefore used three different fluorescent dyes (Fig. 1), i.e. positively charged methylene blue (MB), positively charged/zwitterionic rhodamine B (RhB) and negatively charged sulforhodamine B (SRhB). In fact, the study of fluorescence quenching of SRhB by GO has never been conducted, so this is another new interesting information. The interactions between GO and dyes are systematically varied by adjusting the pH of the systems to alter the charges of GO surface and the dye molecules. Although the interactions between GO and MB have been extensively studied, those studies were based on adsorption experiments using UV–vis absorption spectroscopy [19,20]. In some circumstances, however, the condition that maximizes the adsorption does not necessarily maximize fluorescence quenching efficiency [45]. As a result, it is advised that one study fluorescence quenching instead of adsorption for chemical sensing application. The effect of the size of GO sheet on the fluorescence quenching efficiency was also investigated. The results from this work should be useful especially for the design and selection of fluorescent dyes in GO-based fluorescence sensing systems. However, they could also be beneficial to other applications including drug delivery, wastewater treatment and photodegradation.

2. Experimental

2.1. Materials and chemicals

Graphite powder was purchased from Acros Organics. Methylene blue, rhodamine B, sulforhodamine B and fluorescein were obtained from TCI. Potassium permanganate was supplied by Carlo Erba Reagents. Sodium nitrate, sulfuric acid (98% w/w), hydrogen peroxide (30% w/w), hydrochloric acid (37% w/w), citric acid, sodium hydrogen phosphate heptahydrate, potassium dihydrogen phosphate, glacial acetic acid, sodium acetate trihydrate, sodium hydrogen carbonate, sodium hydroxide pellet, acetone and ethanol were purchased from Merck. All chemicals were used as received without further purification. DI water was used in the synthesis of GO whereas Milli-Q water was used in all other experiments.

2.2. Analytical instruments

Absorption spectra were measured by using Agilent 8453 UV–vis spectrophotometer. ATR-FTIR spectrum was recorded on a Nicolet iS10 FT-IR spectrometer. Thermogravimetric analysis was performed by using Perkin–Elmer Pyris 1 TGA. Zeta potentials and particle size distributions were determined by using Malvern Zetasizer Nano ZSP. Fluorescence spectra were acquired on a Varian Cary Eclipse spectrofluorometer.

2.3. Synthesis of GO

GO was prepared via modified Hummers' method [46] with some adaptations. Detailed procedure is described at Supplementary material. The product obtained was characterized by ATR FT-IR spectrometer, UV–vis spectrophotometer, thermogravimetric analyzer (TGA) and zetasizer.

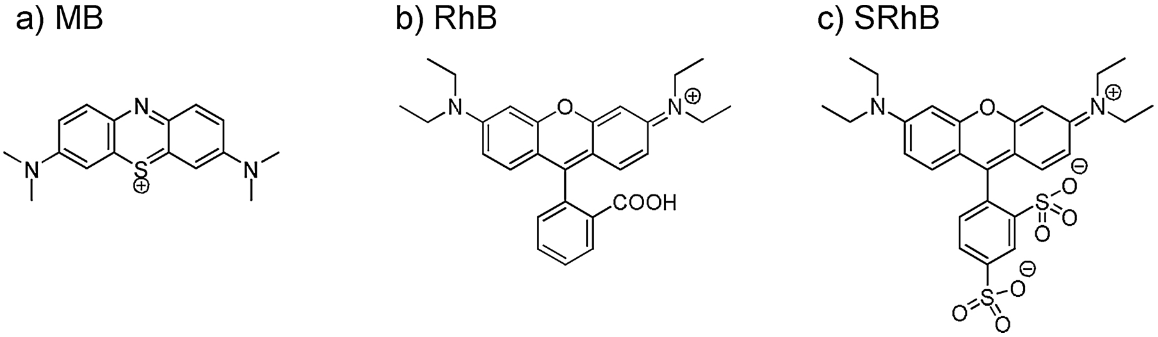

Fig. 1. Chemical structures of (a) Methylene blue (MB), (b) Rhodamine B (RhB) and (c) Sulforhodamine (SRhB).