Solvent induced fluorescence enhancement of graphene oxide studied by ultrafast spectroscopy

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ABSTRACT

Femtosecond transient absorption (TA) spectroscopy combined with picosecond time resolved fluorescence (TRF) were used to reveal the fluorescence kinetics of graphene oxide (GO) in water, ethanol and water-ethanol mixtures. Size-independent fluorescence of GO were observed in water, and pH-dependent fluorescence spectra could be fitted well by a triple emission relaxation with peaks around 440 nm, 500 nm, and 590 nm respectively. The results indicate that polycyclic aromatic hydrocarbons (PAHs) linked by oxygen-containing functional groups dominate GO's fluorescence emission. GO's fluorescence quantum yield was measured to be 2.8% in ethanol but 1.2% in water. The three decay components fluorescence decay, as well as the transient absorption dynamics with an offset, confirmed this solvent induced fluorescence enhancement. GO's Raman spectral signals showed that GO in ethanol has a smaller average size of PAHs than that of GO in water. Therefore, besides other enhancement effects reported in literatures, we proposed that solvents could also change the size of PAHs, resulting in a photoluminescence enhancement. Our experimental data demonstrates that GO's quantum yield could be up to 2.8% in water and 8.4% in ethanol and this observation may help ones to improve GO's photoluminescence efficiency as well as its applications in solution.

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1. Introduction

Graphene and its derivatives have been reported to have multiple tantalizing prospects or applications in the fields of photochemistry [1,2], catalytic chemistry [3–5], supramolecular chemistry [6], biosensors [7,8], and membranes for molecular separation [9] such as seawater desalination and sewage disposal etc. The pristine graphene is insoluble, but the majority of studies have taken place in liquid media. Thus, the soluble graphene oxide (GO), which is the most important derivative of graphene, has attracted lots of interest due to its unique optical and electronic properties [9–13]. GO is chemically functionalized graphene and it retains graphene-like sp^2 domains, and these domains with plenty of oxygen-containing functional groups, such as hydroxyl (—OH), epoxide (C—O—C), carboxyl group —COOH) and carbonyl group (—C=O). Literatures showed that the intercalated water could change the entire interlayer chemistry in multilayered GO [14]. The water-mediated interactions also play an important role in photoluminescence (PL) emission of GO. For example, the formation of local environment in the GO nanosheet could generate a strong excitation wavelength dependent PL [15]. PL from the surface-modified functional groups in GO have attracted extensive attention, because varying GO's band gap can tune the PL emission range from visible to near-infrared [16,17]. Tunable PL emission of GO can enlarge its applications in optical and bioimaging fields [18,19]. However, the detail role of solvent in these processes has not been established, and only few literatures report the relationship between solvents and GO's PL quantum yield (QY).

Many studies tried to expound the PL mechanism of GO, one of the most popular viewpoints claims that the PL of GO comes from the quasi-molecular fluorophores, which is the sp^2 domains in basal plane surrounded by the oxygen-containing functional groups [20]. Another viewpoint is that quantum dots (QD) like structure induced fluorescence-emission in GO [12]. Based on those two theories, there are many factors (the variety of functional groups in GO nanosheet, the pH value of GO solution, and the types of small aromatic molecular structures linked functional groups) can affect the PL properties of GO in solvents. Moreover, the non-stoichiometric structure of GO and different experimental investigation methods have given rise to controversial results, leading some amount of confusion in the origin of GO's PL.

In this work, fresh GO was synthesized from natural graphite by using a modified Hummer's method as reported previously [21],

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and the most common deionized water (DI, Direct-Q3UV, Merck Millipore) was replaced by other solvents. Then the photoluminescence quantum yield, TA spectroscopy and TRF spectroscopy of GO in several solvents were measured, aiming to explain why GO in ethanol possesses a higher PL quantum yield than in DI.

2. Experimental

2.1. Sample preparation and characterization

Fluorescent GO nanosheets were synthesized from natural graphite powder, details of its physicochemical characterization are reported in the support information file. GO nanosheets in solutions were separated by centrifugation at 3000 rpm during the first step. The centrifugal product was discarded to remove the GO nanosheets with very large sizes (in the scale of micrometer). In the second step, the centrifugal supernatant was separated by centrifugation at the speed of 5000 rpm and the collected centrifugal product was dispersed in solvents. The dynamic light scatter (DLS) method was used to measure the size distribution of GO nanosheets, and the average size is 503 nm (Fig. S3C). We repeated this protocol by using 7000, 9000 and 11000 rpm centrifugation, and obtained GO samples with the sizes of 485, 466 and 357 nm, respectively (Fig. S3D–F). Fig. S1 gives the Fourier transformed infrared (FTIR) and Raman spectroscopy of GO powder. Fig. S2 gives the TEM of GO nanosheets, and the insert picture gives the size distribution of our GO nanosheets.

2.2. Time resolved fluorescence spectroscopy

Fluorescence lifetime was measured by a homebuilt time-correlated single photon counting (TCSPC) system (4 ps per channel and 12,500 channels) with electronics (PicoHarp 300 from Picoquant, Germany) and a super-continuum pulsed fiber laser (SC400-pp-4 from Fianium, UK). The pulse duration of fiber laser was ∼190 ps. An acousto-optic tunable filter (AOTF) and an OD4 short-pass filter were used to select the excitation wavelength. A monochromator and an OD4 long-pass filter were employed to choose the detection wavelength.

2.3. Femtosecond transient absorption spectroscopy

The transient absorption system was conducted in a femtosecond transient absorption spectrometer (Helios fire, Ultrafast System) with pump probe beams generated from a Ti: Sapphire laser system (Astrella, 800 nm, 100 fs, 7 mJ/pulse, and 1 kHz repetition rate, Coherent Inc.). One section of the fundamental beam was used to generate a white light continuum (WLC) probe beam by focusing into a Sapphire, and the WLC range was from 420 nm to 800 nm. Another section of the fundamental beam was imported into an optical parametric amplifier (OPerA Solo, Coherent Inc.), and the power of the output pump beams was adjusted to ∼0.2 mW by a neutral-density filter wheel to avoid photobleaching. All experiments were carried out at room temperature. The instrument response function (IRF) of this system was determined to be 150 fs by measuring the solvent responses under the same experimental conditions.

3. Results and discussion

3.1. Size-independent fluorescence of GO with multi-peak emission

GO nanosheets with different size were prepared by centrifugation at different rotating speeds. Details of these features are described in the support information file. Fig. S3A shows that all

GO nanosheets possess the same ultraviolet–visible absorption with a peak around 230 nm (π-$\pi*$ electronic transition of the C=C bond in the aromatic ring) and another peak around 305 nm (n-$\pi*$ transition of the C=O bond), respectively. Fig. S3B demonstrates that GO nanosheets with different sizes also have the same fluorescence emission spectra. Moreover, Fig. S4 shows the detailed information of fingerprinting photoluminescence of the functional groups in GO vs. pH values. The spectra can be fitted well by a multiple emission relaxation. Similar phenomenon was reported in several literatures [15,20,22].

Based on the fact of size-independent fluorescence in GO, it can be concluded that GO's PL emission may come from both of QDs and PAHs structures. However, if we consider the fact that GO's multi-peak fluorescence emission was not randomized, it is clear that GO's fluorescence is primarily attribute to the PAHs structure induced emission. Several literatures reported the PAHs structure induced fluorescence-emission of GO [20,22,23]. To be precise, the specific PAHs structure can be described as PAHs linked with oxygen-containing functional groups. Carboxyl group was reported to dominated the fluorescent emission behavior of GO [15]. The emission peak is ∼600 nm. Our results are consistent with those previous results. Therefore, in this work, our molecular model is based on the PAHs linked with carboxyl groups.

3.2. Solvent-induced fluorescence enhancement effect

Under the circumstances above, we carried out the following study. At the beginning, by utilizing ethanol to displace DI water, the fluorescence intensity of GO in solution showed clearly increasing.

Prepared GO samples in the mixed solvents of ethanol and DI have different PL QYs. All samples have the same GO mass and solvent volume, but the volume ratio of ethanol and DI. Fig. 1A gives the steady-state fluorescence spectra of GO in mixed solutions, and the results show that the GO in pure ethanol has stronger fluorescence emission than that in pure DI. In Fig. 1B, it shows the QYs of GO vs. ethanol ratio in solution, and it has a linear correlation. GO's QY is measured to be 2.8% in pure ethanol in our experiment, but only 1.2% in pure DI.

It has been reported that GO can be regarded as a kind of solid acid, and the ionization of GO plays an important role in its PL emission [15,22]. The reported GO protonation equilibrium can be described as following: GO + H⁺ ⇌ protonated GO. In our experiment, the mass fraction of GO could not be precisely measured, but all the samples were prepared by diluting the sticky GO gel with solvents. It is easy to process the solvent replacement with the sticky GO gel by centrifugation.

It is noticed that GO's behavior of ionization equilibrium is analogous to that of strong acid. Fig. 2 shows UV–Vis absorption at 230 nm vs. the hydrogen ion concentrations during the dilution process of GO in DI environment. In this situation, the mass fraction is inversely proportional to the volume, and both the UV–Vis absorption and the hydrogen ion concentrations have the same relationship with the volume. Insert in Fig. 2 gives the direct relationship between UV–Vis absorption and the hydrogen ion concentrations. It is illustrated that dilution cannot change GO's behavior of ionization equilibrium, and GO in DI should have the same hydrogen ion quantity. Here, it is worth to point out that we cannot lead to the definitive conclusion that DI molecules do not affect the protonation equilibrium of GO, but the statement that GO at low concentrations (UV–Vis absorption in the range of 0.3–1.0 OD at 230 nm) should have the same ionization equilibrium is appropriate. Actually, in the solvent of ethanol, methyl alcohol, we could obtain the same conclusion. This can be explained that single layer GO in such a concentration range is well-dispersed without any intermolecular or intramolecular interaction [14,24], which means the