Imaging and spectrum of monolayer graphene oxide in external electric field

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ABSTRACT

The recent boom in sensor and optical materials based on graphene oxide (GO) requires the improvement and control of its optoelectronic properties. Here, we report the imaging and spectrum of transmission and fluorescence for monolayer graphene oxide (mGO) in an external electric field. It is demonstrated that the image of mGO reveals pronounced spatial heterogeneity under an electric field, and the spectrum presents electrically reversible modulated features. We explain these phenomena by the electric-field-induced changes of electronic density of localized states (DOLS), and we perform the calculations for DOLS by using the first-principles density functional theory.

1. Introduction

Following the exciting studies on graphene [1–3], chemically derived graphene oxide (GO) [4–6] has attracted a considerable amount of attention in recent years, because it is the main precursor in graphene synthesis [7,8] and due to its the huge potential applications in biosensing [9], energy storage [10,11], and nonlinear optics [12,13]. To date, fluorescence sensors [14,15], supercapacitors [16], and laser absorption media [17] based on GO have been reported.

Considerable number of studies have focused on the structure and chemistry of GO [6,18,19]. In particular, the oxygen-containing functional groups in GO have been determined by spectroscopic techniques. The results have shown that the hydroxyl (C–OH) and epoxy groups (C–O–C) are on the basal plane whereas small amounts of carboxyl (C–COOH) and carbonyl (C=O) are at the sheet edges [8]. Vast holes in the basal plane have also been observed by utilizing ultra-high-resolution transmission electron microscopy [20]. It is concluded that the sp² clusters formed by graphite carbon atoms and the sp³ clusters consisting of functional groups, holes, and other defects coexist in the GO plane. However, the chemically inhomogeneous and spatially disordered GO structures result in poor optoelectronic properties [21]. Many attempts have been made to improve and control its characteristics, such as chemical and photocatalytic reduction [22,23], thermal annealing [21], and solvent effect [24].

An external electric field (EEF) has been used to manipulate the optoelectronic properties of multilayer GO films efficiently. In 2011, Ekiz et al. observed the reversible reduction and oxidation of multilayer GO films under an electrical stimulus [25]. Later, Ciraci et al. investigated the effects of EEF on the oxidation/deoxidation of GO as absorption/desorption of oxygen atoms from epoxy groups by first-principles
calculations [26]. In 2012, Hu et al. studied the electrically controlled electron transfer of thionine-functionalized reduced GO multilayer films [27].

Compared with multilayer GO, the advantage of monolayer GO (mGO) is the abundantly detectable optical properties, which removed the averaged effects. However, to our knowledge, research on the control of the optical properties of mGO has not been reported yet. In this work, we manipulate the optical properties of mGO films by EEF. It is found that the images of transmission and fluorescence reveal pronounced spatial heterogeneity of mGO, and their spectra are shown to be reversibly modulated.

2. Experimental

GO (dispersion in water, 0.5 mg/ml), purchased from Sigma-Aldrich, was synthesized by the modified Hummers method with a carbon ratio of 50% determined by X-ray photoelectron spectroscopy (XPS). The GO dispersion was diluted to a concentration of $5 \times 10^{-3}$ mg/ml with deionized water, and then 100 µL of the GO dispersion was spin-coated (3000 rpm) onto a glass coverslip. The as-prepared GO film was dried in vacuum at 25°C for 24 h to remove the remaining solvent.

The fluorescence and transmission spectra of mGO were measured using a home-built scanning confocal microscope (Fig. S5), which was based on an inverted microscope (Nikon, ECLIPSE TE2000-U) [28]. The 635-nm CW diode laser (PicoQuant, PDL808), coupled with an acoustic optical modulator (AOM, Crystal Technology, AA-80-B46) with a modulating frequency of 50 MHz, was used to excite the mGO sample. The output of the modulated laser was split into two optical paths by a 90/10 beam splitter. The weaker laser beam (10%), used to monitor the laser power fluctuation, was detected using a photodetector (PD, Femto, HSA-X-S-1GB-SI-FS). The higher power laser beam (90%), after passing through an attenuator and a quarter-wave plate, was transmitted through an optical fiber and collimated by a beam expander. Then the laser beam was directed by a dichroic mirror (Semrock, Di01-R635-25·36) towards the back aperture of an oil immersion objective (Nikon, NA = 1.3, 100×). The objective was used to focus the beam to a diffraction-limited spot onto the sample, which was placed on the piezoelectric nanometer translation stage (Tritor, 200/20SG). The transmission light through mGO sample was detected by another PD (Femto, HCA-S-400M-SI-FS). Meanwhile, the fluorescence from the mGO sample was collected by the same objective. After passing through the dichroic mirror, a notch filter (Semrock, NF03-633E-25), and a band-pass filter (Semrock, FF01-642/LP-25-D, 690–710 nm) to block the backscattered laser and background, the fluorescence was further filtered spatially by a 100-µm pinhole and detected by a single photon detector (PerkinElmer, SPCM-AQR-15).

Confocal fluorescence imaging was acquired by raster-scanning the mGO sample in the focal plane, and the fluorescence intensity was recorded for each imaging pixel. The signals arising from both PDs were inputted into lock-in amplifiers (Stanford Research, SR830) for demodulating. The demodulated signals were then digitized by a data acquisition card (National Instrument, NI 6251).

3. Results and discussion

The atomic force microscopy (AFM) image of a typical GO sample is shown in Fig. 1. The thickness of the resulting GO sample is about 1.5 nm, which corresponds to the structure characterization of mGO [18].

Typical transmission and fluorescence images are shown in Fig. 2. Fig. 2a–d are the transmission images for a piece of mGO with an area of $6 \times 6 \mu m^2$ under an EEF of 0, 750, 750 V/mm, and the recovered 0 V/mm, respectively. The corresponding fluorescence images are shown in Fig. 2e–h, respectively. The various colors in these images indicate notable changes in transmission and fluorescence intensities. It can be found in Fig. 2 that both absorption and emission images exhibit spatial heterogeneity for the mGO sample with and without EEF. As there are many $sp^3$ clusters isolated by the graphitic $sp^2$ clusters in mGO [6], the anisotropic optical properties would arise from the heterogeneous surrounding environments of $sp^3$ clusters. Hence, the transmission images reveal various features for different domains on the mGO.

Fig. 1 – (a) A $4 \times 4 \mu m^2$ AFM image of monolayer graphene oxide (mGO) deposited on a glass coverslip. (b) The height data of the selected red dashed line. (A color version of this figure can be viewed online.)
Fig. 2 – Transmission images of mGO film under external electric fields (EEF) of (a) 0 V/mm, (b) 750 V/mm, (c) −750 V/mm, and (d) the recovered 0 V/mm, respectively. (e)–(h) Represent the corresponding fluorescence images, respectively. The units for the transmission intensity and fluorescence intensity are millivolts and counts per second (cps), respectively. The domains D1, D2, and D3 plotted as triangle (∆), circle (○), and diamond (□) are chosen to show the detailed changing patterns of GO under different EEF strengths. (A color version of this figure can be viewed online.)
When the EEF is applied onto the mGO sample, each domain exhibits distinct changing patterns. To analyze in detail, three domains D1, D2, and D3 are selected, which are marked with a triangle ($\triangle$), a circle ($\bigcirc$), and a diamond ($\diamond$), respectively. As shown in Fig. 2a, the transmission intensity of D1 under zero EEF is about 2.0 mV, which shows a strong absorption compared to the background of 4.0 mV in transmission images, as shown in Fig. 2a–d. When the EEF is applied, the transmission becomes stronger, such as 3.0 mV for 750 V/mm as well as 4.0 mV for 1.0 kV/mm. (A color version of this figure can be viewed online.)

**Fig. 3** – (a)–(c) are transmission and fluorescence spectra as a function of the triangular wave EEF for spots S1, S2, and S3. Those spots are located in the domains D1, D2, and D3, respectively. The EEF is periodically swept between −1.0 and 1.0 kV/mm. (A color version of this figure can be viewed online.)
−750 V/mm, respectively. In this case, the phenomena reveal that absorption becomes weaker. Correspondingly, the fluorescence intensity varies from 4.0 kcps for 0 V/mm to ~3.0 kcps for ±750 V/mm, as presented in Fig. 2e–g. When the EEF returns to 0 V/mm, the transmission recovers to 2.0 mV, and the fluorescence also recovers to its initial intensity. Conversely, the response of D2 is opposite to D1 under EEF. Initially, the transmission is about 4.0 mV, indicating very weak absorption, as shown in Fig. 2a. Then the intensities decrease to 3.0 mV for 750 V/mm and 2.0 mV for −750 V/mm, and they recover to 4.0 mV when the field is turned off. As a result, the absorption intensity for D1 is decreased with increasing EEF, whereas the intensity is increased for D2. There also existed some domains that show an inconspicuous response to the EEF, such as D3.

To study the optical properties of the mGO sample, we focused the laser on the selected spots while applying alternating EEF. The lateral dimension for the selected spot is decided by the laser spot diameter, which is about 300 nm determined by the diffraction limit. The EEF in the region of −1 to 1 kV/mm is controlled by a triangle wave with a frequency of 0.2 Hz. Fig. 3a presents the electric-field-dependent transmission and fluorescence spectra for spot S1 chosen from domain D1. Note that the increase (or decrease) in the transmission (or fluorescence) intensity as a function of the applied field. The transmission is enhanced from 2.1 to 4.2 mV with the EEF increasing from 0 to ±1 kV/mm. Meanwhile, the fluorescence is completely quenched. Due to the heterogeneity of mGO, some spots exhibit opposite behavior compared with spot S1, as shown in Fig. 3b. The transmission of spot S2, chosen from domain D2, decreases from 6.4 to 4.8 mV and the fluorescence increases from 10 to 20 kcps as the EEF increases from 0 to ±1 kV/mm. This indicates that the transmission decreases about 25% under EEF, whereas the fluorescence increases twice, respectively. In addition, the results suggest that the variation of the optical response is reversible along with periodic field. It is found that the reversible behavior could repeat for >100 cycles (about 1 h), as shown in Fig. S1, which is much more than that in multilayer GO with just several cycles [25]. Moreover, the modulated depths of transmission light in mGO are significantly improved compared with that in graphene of about 1.5% [29].

When the electric field strength is smaller than a specific value, which is defined as the characteristic electric field, there is no change in the transmission and fluorescence spectra. It can be observed that the characteristic electric field for spot S1 is about 0.5 kV/mm, whereas it is 0.8 kV/mm for spot S2, which is significantly larger, as shown in Fig. 3a and b, respectively. As a consequence, both transmission and fluorescence spectral profiles for spot S2 are narrower than that for spot S1. The different characteristic electric fields and spectral shapes would also reveal the anisotropic optical properties of GO.

The results for both spots S1 and S2 show that the altered optical properties of mGO are independent of the direction of EEF. However, some spots present EEF-direction-dependent change, such as spot S3 selected from domain D3, as shown in Fig. 3c. Although the transmission spectrum is enhanced in both directions, the spectral profiles are much wider in the positive field than that in the negative field. The characteristic field in the positive-going direction is about 0.2 kV/mm, whereas it is 0.6 kV/mm in the negative-going direction. In addition, the transmission is increased from 2.6 to 3.2 mV under the positive field, while it is just enhanced to 2.9 mV under the negative field. Correspondingly, the quenching fluorescence spectra show asymmetry when the mGO is under bipolar (positive and negative alternately) EEF. The results show that the local optical properties are more sensitive to the magnitude of EEF in the positive-going direction.

As suggested by Shang et al. [30] the localized states of GO could be originated from the Anderson localization of electronic wave functions in the heterogeneous and disordered sp²/sp³ complex structure, which contributes to the unique optical properties. It is demonstrated that electron-hole recombination from the bottom of the conduction band (CB) and nearby localized states to wide-range valance band (VB) was the origin of the fluorescence of GO [31]. Gokus et al.

![Fig. 4 – Schematic diagram of excitation of mGO by 635-nm laser with and without EEF, respectively. The pink parts and blue parts represent the conduction band (CB) and valence band (VB), respectively. (a) and (b) are the electric density of localized states (DOLS) for mGO without and with the EEF. Red arrows denote the electronic transitions from VB to CB within mGO during the excitation. (A color version of this figure can be viewed online.)](image)
assigned the strong photoluminescence in oxygen plasma-treated graphene to CO-related localized electronic states of oxidation sites [32]. Chien et al. and Eda et al. suggested that the disorder-induced states formed by a boundary of oxidized sp\(^3\) carbon clusters directly influence the distribution of density of localized states (DOLS) [33,34]. Therefore, the evolution of transmission and fluorescence spectra of mGO could be explained based on the changes of DOLS under EEF.

mGO consists of abundant oxygen-containing polar functional groups. The polar groups with nonuniform type and coverage result in small sp\(^2\) carbon clusters isolated by the oxidized sp\(^3\) carbon clusters [35]. When the EEF is applied, the charge distribution will vary due to the induced dipole moment of polar groups. As a consequence, DOLS would be changed by EEF. Therefore, the polarity effects of functional groups in EEF would lead to the various responses of absorption and emission.

The schematic diagrams for the changes of DOLS under EEF are shown in Fig. 4. The pump laser with the energy of \(~1.95\ eV (~635\ nm)\) excites the electrons from the VB to the localized state nearby the resonance energy level in CB. When the EEF is applied on mGO, the DOLS in CB formed by sp\(^3\) clusters changes with the polarity effect of polar groups; therefore, the DOLS corresponding to the laser resonance will become bigger or smaller, as shown in Fig. 4. Thus, the absorption and emission intensities would be varied by the EEF, which arise from the changes in the DOLS of mGO films. Similarly, the characteristic electric fields also reflect the critical polarity effects in mGO.

We have performed the calculations for DOLS by utilizing first-principles density functional theory (DFT) [36,37]. In a previous study, Wang et al. [38] determined the energy diagram of GO with the first-principles theory. The results indicated that the epoxy and hydroxyl groups prefer to aggregate along the armchair direction and form stable one-dimensional chain configurations on the basal plane. Meanwhile, one can define the coverage of the functional groups (R) as follows:

\[
R = \frac{\text{number of sp}^3\text{C}}{\text{total number of C atoms}} \times 100\% \tag{1}
\]

Here the sp\(^3\) carbon (C) indicates the connected bonds with hydroxyl (C–OH) and epoxy groups (C–O–C), because our experimental sample gives carbon (C):oxygen (O) = 2.1:1; a stable GO structure with R = 50% and C–OH:C–O–C = 1:1 is discussed here. We construct the mGO model based on the supercell \((C_{48}O_{16}H_8)\) with \(2 \times 12 \times 1\) units containing 72 atoms for DFT calculations. In order to play for eye, the \(10 \times 12 \times 1\) supercells are shown in Fig. 5a, which are multiplied five times of the supercell along the x-axis. The GO sheet is

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![Fig. 5 – Atomic structural models and DOLS of mGO with R = 50% and hydroxyl (OH):epoxy (O) = 1:1 under (a, b) unpolarized, (c, d) positively polarized, and (e, f) negatively polarized, respectively. The red balls represent oxygen (O) atoms, gray balls represent carbon (C) atoms, and the light blue balls represent hydrogen (H) atoms. Here, the polarized case is realized by, respectively, moving O and H atoms about 0.18 and 0.21 Å along the [010] direction and [0 − 10] direction. To view the atomic displacements more clearly, the enlarged partial views of the models are shown as pointed by the arrows. (A color version of this figure can be viewed online.)](image-url)
simulated with a vacuum thickness of 15 Å, which is enough to decouple the adjacent sheets. DFT calculations are performed by means of the Vienna ab initio simulation package (VASP) [39] with the Perdew–Burke–Ernzerhof approximation [40] to the exchange–correlation functional. The k-point mesh in the full wedge of the Brillouin zone (BZ) is sampled by a \(21 \times 3 \times 1\) grid according to the Monkhorst–Pack (MP) [41] scheme. A cutoff energy of 1000 eV is used for the set of plane waves. In all calculations, self-consistency is achieved with a tolerance in the total energy of at least 0.01 meV. The calculated result without an electric field is shown in Fig. 5b. A band gap of about 0.7 eV is observed for our present model, and the DOLS in both CB and VB are shown.

It has been demonstrated that the atomic displacements for GO under an electric field exist [26,42]. Here, we moved the –O and –OH groups from their equilibrium sites with 0.18 and 0.21 Å along the [010] and [0 −10] direction to simulate the electronic-field-induced polarity effect, as shown in Fig. 5c and e. As a consequence, the localized states in both CB and VB are successfully manipulated (Fig. 5d and f).

Because the optical properties of mGO are exactly dependent on the –O and –OH groups from their equilibrium sites with 0.18 and 0.21 Å along the [010] and [0 −10] direction to simulate the electron–field-induced polarity effect, as shown in Fig. 5c and e. As a consequence, the localized states in both CB and VB are successfully manipulated (Fig. 5d and f).

3. Conclusions

Our experimental results have demonstrated that the transmission and fluorescence images reveal the anisotropic optical features of mGO, which can be manipulated by EEF. Both the transmission and fluorescence spectra can be modulated by EEF. The modulation depth in the transmission spectrum could be up to 25%, and the fluorescence spectrum of mGO could be quenched completely or enhanced several times under EEF. Theoretical analysis suggested that the modulated spectra under an electrical stimulus were attributed to the polarity effect of oxidized sp³ clusters, which caused the changes of DOLS in mGO films. Furthermore, the reversible feature under periodic EEF is observed in both transmission and fluorescence spectra. The results exhibit huge potential applications in the design of novel optoelectronic devices, GO-based fluorescence sensors, and molecular electronics.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2015.05.106.

R E F E R E N C E S


