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Observing and tuning the density distribution of localized states of monolayer graphene oxide by using external electric field

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The density distribution of localized states (DDLS) in monolayer graphene oxide (mGO) was observed and tuned under applied external electric field. The fluorescence anisotropy in mGO basal plane was observed which revealed the inhomogeneous DDLS. The enhanced and/or quenched fluorescence trajectories under electric field demonstrated the tuning of DDLS. Using the first-principles density-functional calculations, we demonstrated that the DDLS tuned by electric field could be attributed to the polarity effect of oxidized sp2 functional groups. The tunable DDLS is beneficial to improve and control the mGO’s optoelectronic properties.

Following the abundant researches of graphene,1 the graphene oxide (GO) has also received great attention due to its promising applications2 in biosensing,3 optics device,4 and energy storage.5,6 To date, GO-based fluorescence-sensor,7 laser absorption medium,8 and supercapacitor9 have been demonstrated.

GO is a hybrid material which contains both conducting π-states from sp2 carbons and insulating oxidized sp2-bonded carbons with large energy gap.10 As a consequence, a large number of disorder-induced localized states are formed by the disordered oxygen-containing functional groups attached to the carbon atoms, which result in the unique optical properties of GO.11 Therefore, the GO’s detectable optical properties are much plentiful based on the type and coverage of functional groups in the basal plane. Luo et al.12 proposed that the bond distortions arising from the density distribution of localized states (DDLS) were contributed to the fluorescence of GO. Gokus et al.13 assigned the strong photoluminescence in oxygen plasma treated graphene to CO-related localized electronic states of oxidation sites. Shang et al.14 investigated the fact 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. Besides, the changes of DDLS could induce the variation of fluorescence, Eda et al.15 studied that the photoluminescence of chemically derived GO was varied with hydrazine-reduction treatment. Chen Group16 reported that the localized states, formed by boundary sp3 domains transforming to non-oxidized sp2 domains, would directly influence the emission properties.

The differential conductance measurement and capacitive photocurrent spectroscopy have been used to determine GO’s DDLS. By fabricating tunneling junction devices with reduced graphene oxide (rGO) sheets, Wang et al.17 obtained rGO’s DDLS by measuring the differential conductance of rGO in a wide voltage range. Later, Li et al.18 demonstrated the fluctuations of the local density of states by determining the quantum capacitance of the top-gate graphene devices. Besides, Bansal group19 measured the DDLS of GO by means of capacitive photocurrent spectroscopy, and unraveled that energy peaks in DDLS were correlated with the luminescence of GO. Comparing to these measurement for multilayer GO, the DDLS detection for the monolayer GO (mGO) could remove the ensemble averaged effects. However, the observing of DDLS by fluorescence in mGO, as well as the direct tuning of DDLS by external stimulus has not been reported till now.

In this letter, we investigated the GO’s DDLS by scanning confocal fluorescence imaging with sub-micrometer resolution determined by the diffraction limit. It was shown that DDLS in mGO could be observed and tuned by applying external electric field.

GO was purchased from Sigma-Aldrich (Product number: 763705, dispersion in water, 0.5 mg/ml, Carbon ratio: 50%) and synthesized by modified Hummers method.20,21 After diluting, 100 μl GO dispersion with concentration of 5 × 10−3 mg/ml was spin-coated onto a glass cover slip. The as-prepared GO sample was dried at room temperature in vacuum conditions for 24 h to remove the remaining solvent. According to atomic force microscopy (AFM) image, as shown in Fig. 1, the thickness of the main resulting GO sample was about ~1.5 nm, corresponding to the structure characterization of monolayer.22 The two-terminal electrodes consisted of thin aluminum and separated by 2 mm were fabricated on the glass substrate.

We collected the fluorescence of mGO based on a home-built scanning confocal fluorescence microscope system which had been described in Ref. 23. Here, the lateral dimension of laser spot was about 300 nm determined by the diffraction limit. Typical fluorescence images were shown in Fig. 2, where the fluorescence of a block of mGO with about 20 × 20 μm area under the field of 0, 1000, and the recovered

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0 V/mm were presented, respectively. The colors in these images indicated the wide variability in fluorescence intensities, which revealed the anisotropic DDLS in mGO. As there were lots of small sp^3 clusters isolated by the various graphitic sp^2 clusters, the DDLS—rooted in mGO’s chemically inhomogeneous and spatially disordered structures—were wide variability arising from the anisotropy of sp^3 cluster’ surrounding environments. As the fluorescence was correlated to the DDLS as mentioned above, the emission would perform various features for different domains on mGO plane even without electric field, as presented in Fig. 2(a). With the electric field applied, the oxygen functional groups were polarized, leading to the changes in DDLS which directly influenced fluorescence emission, as shown in Fig. 2(b). After removing the electric field, the fluorescence image recovered to the initial appearance, as presented in Fig. 2(c).

To investigate the characteristics of DDLS in mGO under the external electric field, we detected the fluorescence trajectories with focusing the laser on the selected spots, meanwhile applying the alternating voltage on the electrodes. The fluorescence enhanced trajectories tuned by the electric field for four spots (A, B, C, and D, respectively) selected from Fig. 2(a) were shown in Fig. 3. The left part (in orange) presented a stable fluorescence signal with the electric field absent. The middle part (in blue) was the fluorescence intensities varying as the electric field rising from 0 to 1000 V/mm, and the right part (in purple) was the fluorescence varying as the electric field falling from 1000 to 0 V/mm, respectively. Note that the fluorescence trajectories were symmetric and reversible within the rising and falling electric fields.

As shown in Fig. 3(a), no obvious change could be observed until the electric field was raised to 600 V/mm; the fluorescence was enhanced from the initial intensity 5.5 kcps to the maximum 41 kcps at the electric field of about 867 V/mm, while the background was ~500 cps. Here, we defined the characteristic field as the electric field where the fluorescence was tuned to the maximum or minimum, and the tuning depth \( \eta \) as \( \left| \left( I_{\text{run}} - I_{\text{bac}} \right) / \left( I_{\text{ini}} - I_{\text{bac}} \right) \right| \), where \( I_{\text{run}} \) was the maximum or minimum tuned fluorescence intensity, \( I_{\text{ini}} \) and \( I_{\text{bac}} \) were the initial fluorescence intensity and the background, respectively. Here, the characteristic field and tuning depth for peak A were 867 V/mm and 8.1, respectively. Due to the anisotropy of the type and coverage of the oxygen-containing functional groups in selected spots (and also their surrounding environments), the non-uniform tuned results were presented, as shown in Figs. 3(b)–3(d), where all the three spots have two peaks in rising electric field process. Fig. 3(d) exhibited that the profiles of the two peaks (D1 and D2) were remarkable alike with the characteristic fields of 451 V/mm and 789 V/mm, respectively; while Fig. 3(c) showed two distinct peaks (C1 and C2), either full width at half maximum (FWHM), or tuning depths. By the way, the various FWHM also indicated the anisotropic DDLS in mGO. The comparisons for the characteristic fields, FWHM,
and tuning depths for these four spots were presented in Table I.

In the experiment, the fluorescence with inconspicuous responses or quenched results was also determined. As shown in Fig. 4(a), the fluorescence intensity of mGO was uniformity with and without electric field, which revealed the spot N selected from Fig. 2(a) might be located in the mGO plane with less oxygen-containing functional groups, and showed lowly polarity sensitive to the external electric field. The quenched results were presented in Figs. 4(b) and 4(c). The fluorescence in these two spots (E and F selected from Fig. 2(a)) was quenched as a symmetric valley, but had different characteristic fields and tuning depths. The hybrid result for enhanced and quenched fluorescence trajectory could be found in Fig. 4(d); it was clear that the fluorescence trajectory of spot G selected from Fig. 2(a) which was enhanced as a peak (G1 or G1') at the beginning, and then quenched at the 801 V/mm as a valley (G2 or G2'). The comparisons for the characteristic fields, FWHM, and tuning depths for these three selected spots were presented in Table II. The enhanced and quenched fluorescence were both attributed to the tuning of the DDLS in mGO, arising from the polarity effect of oxidized $sp^3$ functional groups in the selected spots. The oxygen functional groups in these selected spots may have different type, number, and coverage; therefore, the optical responses to the electric field between these spots were different.

Since the mGO fluorescence is considered as the electron-hole recombination from bottom of CB and nearby localized electronic states to VB, and also the fluorescence is proportional to the absorption and quantum yield, the experimental results could be explained using the standard description for electron band-to-band transitions. The fluorescence signal $I_{\text{fluo}}$ is proportional to the product of the initial and final localized states integrated over all possible transitions for the excitation energy $h\nu$, which can be expressed as

$$I_{\text{fluo}} = \int_{E_H}^{E_H+E_{BG}-h\nu} \kappa(E) \cdot \Phi(E) \cdot [D(E)D(E+h\nu)]dE,$$

where $D(E)$ is mGO’s DDLS in VB, $D(E+h\nu)$ is the DDLS in CB, $E_H$ is the highest localized state in VB, $E_{BG}$ is the band gap of mGO, $\Phi(E)$ is the quantum yield, and $\kappa(E)$ is a proportionality. The excitation energy $h\nu$ in our experiment is 1.95 eV ($\lambda = 635$ nm). To simplify the analysis, we propose that the quantum yield and the probability for all possible transitions are independent on the external electric field (That is to say, $\Phi(E)$ and $\kappa(E)$ are held as constants to all electric fields here.) When the DDLS (i.e., $D(E)$ and $D(E+h\nu)$) are tuned by external electric field, the fluorescence intensity would be changed.

We calculate the DDLS of mGO with and without field by utilizing the first-principles density functional theory (DFT), respectively. When the DDLS is performed under external electric field, the polarity effect which will induce
the functional groups moving from their equilibrium sites is considered. The atomic structures of mGO’s are rather complicated and exceed the topic of our present study. Considering that the GO sample gives C:O = 2.1:1, here, we only discussed the stable mGO structure with R = 50% and OH:O = 1:1.

DFT calculations are performed by means of the Vienna ab initio simulation package (VASP)\textsuperscript{25} with the Perdew-Burke-Ernzerhof approximation\textsuperscript{26} to the exchange-correlation functional. A cutoff energy of 1000 eV is used for the set of plane waves. The mGO sheet is simulated with vacuum thickness of 15 Å, which is enough to decouple the adjacent sheets. The size of the ordered mGO system (C\textsubscript{48}O\textsubscript{16}H\textsubscript{8}) is 2 x 12 x 1 with 72 atoms in the whole slab model. The k-point mesh in the full wedge of the Brillouin zone (BZ) is sampled by 2 x 3 x 9 grid according to the Monkhorst-Pack (MP)\textsuperscript{27} scheme. In all calculations, self-consistency is achieved with a tolerance in the total energy of at least 0.01 meV.

As shown in Fig. 5(b), a band gap of about 0.7 eV is observed for our present model and the localized states in the VB and CB are clear. After moving the O and OH groups 0.18 and 0.21 Å from their equilibrium sites along the [0–10] direction, respectively, as shown in Fig. 5(c), which is used to simulate the electric field induced polarity effect, the DDLS (i.e., D(E) and D(E + hν) in Eq. (1)) are successfully tuned, as shown in Fig. 5(d). In this case, the fluorescence intensity will be varied. The degree for the functional groups moving from their equilibrium sites under altering electric field would be different; therefore, the tuning depths of D(E) and D(E + hν) would vary as the electric field, resulting in characteristic peaks in fluorescence trajectories. On the other hand, due to the anisotropy of the selected spots, their fluorescence trajectories under electric field are also changeful. When the tuning depth is extremely small, the fluorescence exhibited no obvious response to the electric field, as shown in Fig. 4(a). When the tuning depth is greater than one (and when the integrate value of Eq. (1) becomes larger), the fluorescence is enhanced (as shown in Fig. 3), while if tuning depth is less than one and the integrate value becomes smaller, the fluorescence is quenched (as shown in Figs. 4(b) and 4(c)).

In conclusion, we described an experimental observing and tuning mGO’s DDLS by means of scanning confocal fluorescence microscopy under external electric field. Fluorescence images revealed the mGO’s anisotropic DDLS; the enhanced and quenched fluorescence trajectories demonstrated the different characteristic fields as well as tuning depths between selected spots. DFT calculations confirmed that the variations of DDLS in GO were derived from the polarity effects of functional groups under electric field. The electric-field-tuned DDLS in mGO exhibits huge potential applications in the design of novel optoelectronic devices, laser medium, and GO-based fluorescence sensors.

| Spots | Peaks | CF (V/mm) | ΔF (V/mm) | η |
|-------|-------|-----------|-----------|---|
|       | E     | F         | G\textsubscript{1} | G\textsubscript{2} |
|       | 780   | 587       | 273       | 801 |
|       | 411   | 499       | 240       | 378 |
|       | 0.14  | 0.28      | 1.75      | 0.21 |

FIG. 4. (a) was the fluorescence trajectory of spot N in Fig. 2(a) with inconspicuous responses under electric field, (b) and (c) were the fluorescence quenching trajectories, and (d) was the hybrid result for enhanced and quenched fluorescence trajectories for the three spots (E, F, and G, respectively) selected from Fig. 2(a) as the electric field rising from 0 to 1000 V/mm, and then falling from 1000 to 0 V/mm, respectively. The solid line (green blue and red) indicated the Gaussian fit results.
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