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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 sp^2 clusters formed by graphite carbon atoms and the sp^3 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

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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 5×10^{-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

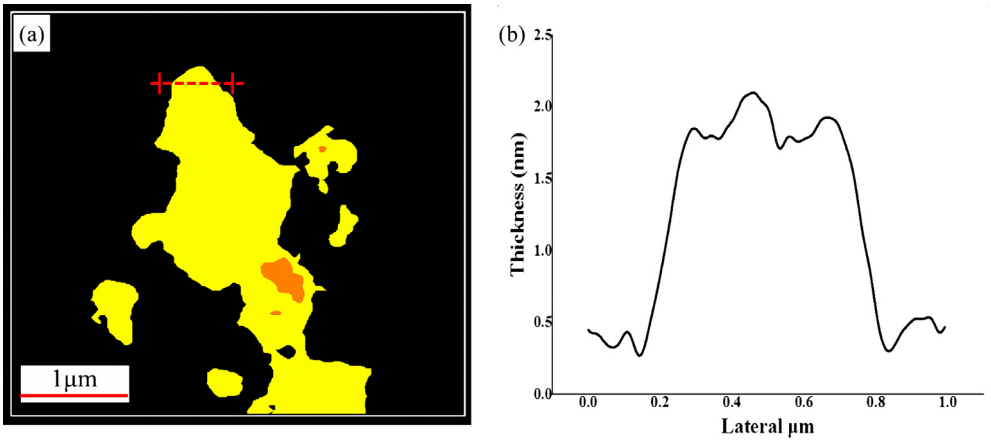

Fig. 1 – (a) A $4 \times 4\ \mu m^2$ AFM image of monolayer graphene oxide (mGO) deposited on a glass coverslip. (b) The height data of the selected red dashed line. (A color version of this figure can be viewed online.)