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Letter to the editor

Rupture index: A quantitative measure of sub-micrometer cracks in graphene

A B S T R A C T

By weight, graphene is stronger than steel; but the monolayer does crack with improper handling. Here, we introduce 'rupture index' as a parameter that quantifies the size and the density of cracks and related defects in graphene. The approach makes use of the high contrast achievable in fluorescence quenching microscopy to distinguish between graphene and the background substrate visible through graphene cracks. Rupture index is the only existing metric for quantifying the amount of cracks in graphene (and other 2D materials) to date; particularly, it serves to quantitatively assess and compare the efficiency of different handling processes, and to quantify the effect of the edges on the global properties (e.g. chemical reactivity, electrical or mechanical performance) of macroscale graphene sheets.

Edges and defects in graphene [1] are ususally characterized using scanning tunneling microscopy [2], transmission electron microscopy [3], electron energy loss spectroscopy [4] and Raman spectroscopy [5] which are all local and hardly provide a quantitative measure of the density and topology of the edges and defects present in a graphene sample. In this article we define "rupture index (RI)", a parameter derived from fluorescence quenching microscopy (FQM) [6–9] to quantify the size and the density of cracks in graphene at the centimeter scale. Graphene quenches the emission of nearby fluorescent dye molecules through non-radiative relaxation of electrons at excited states via a long-range resonance energy exchange mechanism [6,10]. The quenching results in imaging the *shadow* of graphene in fluorescence microscopy [7,8]. In a typical experiment, a graphene sample is spin-coated with PMMA resin containing 2% of fluorescent dye rhodamine B in acetone solution (4 mM). Subsequently, the sample is imaged using a bright field fluorescence microscope to estimate the RI.

The crack quantification approach proposed in this letter is straightforward to use, non-destructive for the sample, fast, automatable and can characterize large area/amount of conductive 2D materials. As the PMMA coatings are commonly used in different graphene manipulation procedures (e.g transferring, electron beam or even optical lithography [11], etc.), the RI measurement can be performed with the same coatings (pre-mixed with fluorophores) without adding any further complexity. Remarkably, RI values are substrate-independent and are compatible with most of substrates used for graphene e.g. SiO_x/Si and glass, without any adjustment required.

Fig. 1 compares the visibility of a selected area of a large graphene sheet (grown in a hybrid cold and hot wall reaction chamber [12]) by means of optical microscopy, scanning electron microscopy (SEM) and fluorescence microscopy. The visibility of graphene is poor in the optical micrograph, improves slightly in the scanning electron micrograph and is the highest in the fluorescence quenching image. The grayscale intensity histogram is plotted below each image featuring sharp and localized intensity distributions for the optical and scanning electron micrographs. The majority of the pixels in the fluorescence micrograph, however, are either very dark (on graphene) or very bright (on cracks), which allow unambiguous distinction of the cracks from the basal plane. This outstanding contrast stems from the fact that the fluorophores can be either 'off' (quenched, close to graphene) or 'on' (emitting, far from graphene) and no intermediate state exist; the situation is very different in the SEM or optical imaging where the presence of crack yields limited contrast compared to the regions covered with graphene.

In order to find the in-plane resolution offered by FQM, we imaged microfabricated graphene ribbons of 1 μm, 2 μm and 3 μm widths (Fig. 2a and b). Plotting the grayscale intensity along the dashed line marked in Fig. 2a showed oscillations of the color intensity corresponding to the emission of fluorophores,

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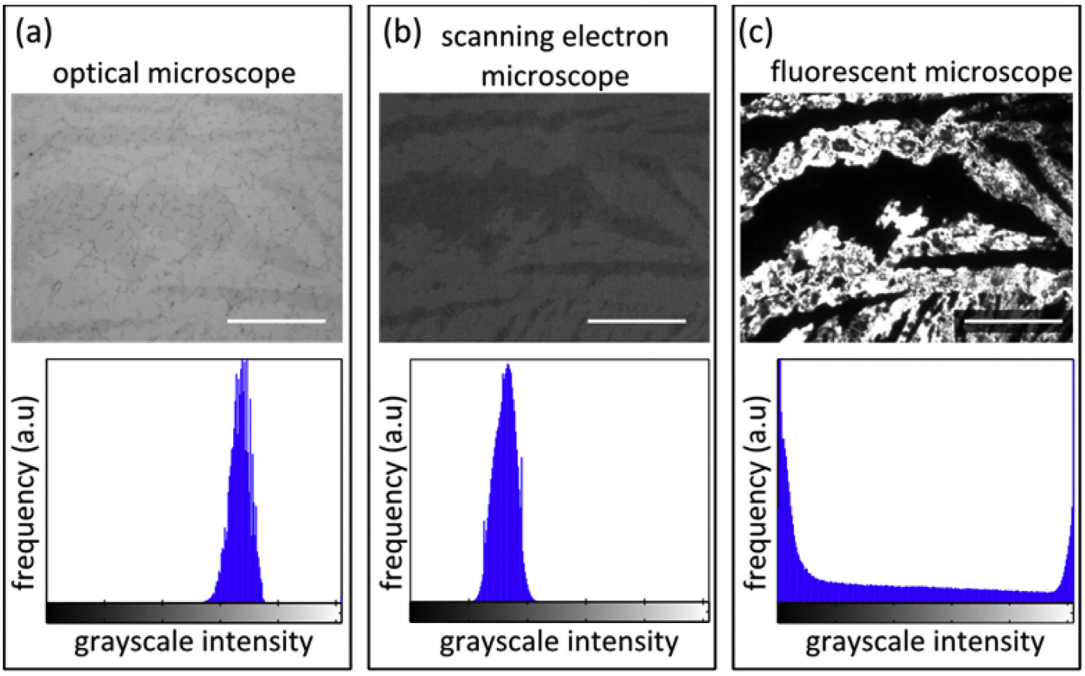

Fig. 1. The efficiency of fluorescence quenching microscopy (FQM) for the visualization of the cracks in graphene. a) Optical image of a cracked graphene area on a SiO_x/Si wafer; **b)** Scanning electron microscope image of the same area; **c)** FQM of the same area; graphene was covered with PMMA mixed with Rhodamin B solution (100:2 ratio). In all the panels, the plot at the bottom shows the histogram of the grayscale intensity of the corresponding image. The optical micrograph is converted to grayscale image to be comparable with the other images; otherwise no further post-processing has been performed. All the scale bars correspond to 50 μm. (A colour version of this figure can be viewed online.)

periodically turned on and off (Fig. 2c). In the overlay plot of the intensity oscillations for the three sets of ribbons, the tangent line at the inflection point revealed a lateral resolution of approximately 650 nm (Fig. 2d). The measured resolution approaches the reported values for the utilized objective [13], highlighting that the resolution limit is imposed by the optical set-up.

The sharp contrast between on/off areas in FQM images allows

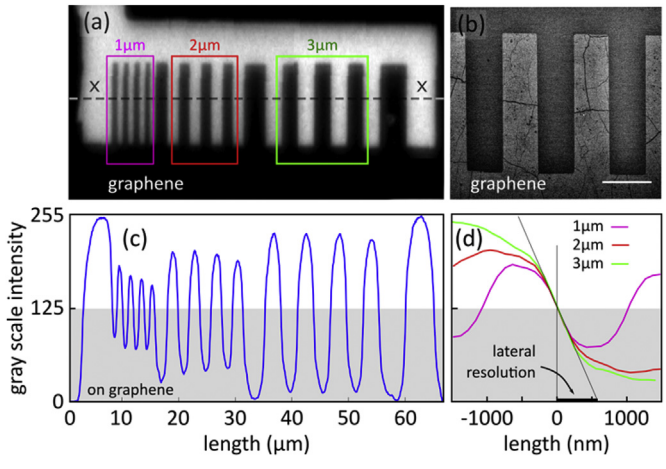

Fig. 2. The lateral resolution of FQM: a) FQM of graphene ribbons with 1 μm, 2 μm and 3 μm widths: For each set, the gap between the ribbons are the same as their widths. **b)** SEM image of the widest ribbons (green window in **a**). The scale bar corresponds to 4 μm. **c)** Grayscale intensity along the line x-x in **a. d)** Overlaid grayscale intensity oscillations corresponding to ribbons of different widths in **c**. The vertical axis has the same unit as in **c**. (A colour version of this figure can be viewed online.)

to numerically assess the density of cracks in graphene. Fig. 3 shows FQM images of three graphene samples transferred onto SiO_x/Si wafers via using: i) a PMMA support [14], ii) a lateral frame and iii) no support. As seen from the fully quenched fluorescence (dark) in the FQM image, the PMMA transfer method prevents graphene to crack (Fig. 3a). For the two other transfer methods, cracks in graphene are clearly visible as white areas (Fig. 3b and c). By automatically counting the pixels (Table 1 and bottom panels in Fig. 3a–c), we define the '*rupture index (RI)*' as the total number of the border (white) pixels divided by the total number of graphene (black) pixels, multiplied by one thousand. As expected, the three different transfer methods yielded different rupture indexes of 1.4 for PMMA transfer, 27.1 for frame-stabilized transfer and 41.5 for the support-free transfer.

The rupture index provides a rough measure of the population of the carbon atoms localized at the edges of graphene. The parameter can be used to assess the influence of the edge sites on global properties (e.g. the chemical reactivity) of graphene. Alternatively in its most simple form of use, the rupture index provides a metric capable of quantitatively ranking different protocols in preserving the integrity of graphene sheets.

Rupture index can quantify the surface related-phenomena. Followingly we measure the efficiency of graphene coatings in preventing metal oxidation. Since the oxidation depends on the area (rather than the perimeter) of the cracks, the definition of the rupture index (now called surface rupture index, RI_S) needs to be adjusted as the total number of the pixels located at the area of the cracks (white) divided by the total number of pixels forming the image (both black and white), multiplied by one thousand. To perform this study, we prepared graphene on copper samples with random RI_S values of RI_S = 3.2, 127.7, 220.8 and 1000 (Fig. 4a, see the Supplementary Information for the details). We studied the correlation of RI_S to the redox behavior of