HIGH-THROUGHPUT IMAGING OF GRAPHENE BASED SHEETS ON ARBITRARY SUBSTRATES AND IN SOLUTION BY FLUORESCENCE QUENCHING MICROSCOPY

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Introduction

Microscopy imaging techniques usually play a critical role in discoveries at small length scales. For example, the discovery that graphene is visible under normal optical microscope when deposited on dielectric-coated silicon wafers has enabled numerous studies on these single atomic carbon sheets [1]. Atomic force microscopy (AFM) is often used to visualize graphene based sheets since it gives accurate thickness value at nanometer scale. However, it has not been made suitable for quick sample examination over large areas due to rather low throughput. Scanning electron microscopy (SEM) can be much faster but it works best for films deposited on conducting substrates. Even though optical imaging of graphene based sheets has been demonstrated by interference technique [1], it requires optimized dielectric thickness and illuminating wavelength. Therefore, alternative methods that can image graphene based sheets on various substrates or even in solution would be very useful for high-throughput sample evaluation. Here we report a general method for visualizing graphene based sheets on arbitrary substrates based on fluorescence quenching. It offers unprecedented imaging flexibility for characterizing graphene based materials.

Experimental

Graphene was prepared by micro-mechanical cleavage method [1]. Graphene oxide (GO) was synthesized using a modified Hummers method [2]. Chemically reduced graphene oxide (r-GO) was prepared by exposing GO-coated substrates to hot hydrazine vapor. To prepare the dye/polymer coating, 1 mg of fluorescein sodium salt powder was added to 10 ml of 1 wt% polyvinylpyrrolidone (PVP)/ethanol solutions. 100 μl of coating solution was then dispensed for each 0.5 in^2 of substrate area, and spun for 5 sec at 300 rpm and then 45 sec at 4000 rpm. The dye/polymer film was also prepared with a photoresist poly(methyl methacrylate) (PMMA) and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM). Fluorescence quenching microscopy (FQM) was performed on a Nikon TE2000-U inverted fluorescence microscope with the Exfo X-cite illumination system using a GFP filter cube.

Results and Discussion

It has been well known that graphitic systems such as carbon nanotubes can strongly quench the emission of nearby dye molecules [3]. Recent theoretical studies showed that graphene should also be a highly efficient quencher [4]. Indeed, Fig. 1A shows that the emission of a fluorescein solution (Fig. 1B, left) can be significantly quenched after adding a small aliquot of reduced GO (r-GO) (Fig. 1B, right) or even GO (Fig. 1B, middle). Fig. 1A inspired us to develop FQM, utilizing emission quenching as a contrast mechanism (Fig. 1C). Typically this can be achieved by spin-coating fluorescein/ethanol solution. PVP was added to the solution to improve the uniformity of the resulting film. Fig. 1D is an AFM image showing a few GO sheets deposited on a SiO_2/Si wafer. Fig. 1E is an as-acquired FQM image of the same area after applying a fluorescein/PVP layer. It perfectly matches the AFM view in Fig. 1D with clear contrast between single and double layers. The dye coating can be easily removed by brief washing after FQM imaging. AFM image of the identical GO sheets after dye removal detected no contamination or change in morphology (Fig. 1F).

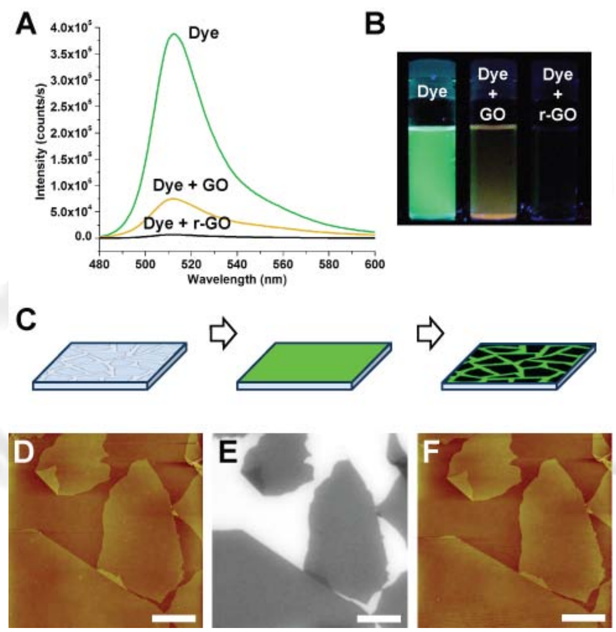

Fig. 1 Visualizing graphene based sheets by FQM. (A) Fluorescence spectra and (B) a camera image showing strong emission quenching by GO and r-GO. (C) In FQM, a dye coating is applied to a graphene covered surface, which upon excitation reveals the underlying sheets. (D) An AFM image of GO sheets deposited on a SiO_2/Si wafer. (E) A FQM image of the same area of the wafer. (F) After washing off the dye coating, no residues can be detected by AFM. All scale bars = 10 μm.

FQM offers unprecedented flexibility for imaging graphene based materials. Fig. 2A is a FQM image of mechanically exfoliated graphene sheets on a SiO_2/Si substrate. The single and multi-layer domains are clearly resolved. Fig. 2B shows a double layer sample prepared by cross-coating a GO monolayer on top of a r-GO monolayer on glass slide. The r-GO sheets indeed appeared darker than the GO sheets, which is consistent with their higher quenching efficiency (Fig. 1A). Fig. 2C shows a spin-coated GO film on a polyester substrate revealing vivid details of the wrinkles and folds of the sheets. On such substrates, GO sheets could not be visualized with optical microscope under reflectance mode (Fig. 2C, inset). FQM is not limited by the wavelength of illumination. Many fluorescent materials are available in case a specific excitation wavelength is preferred. In addition, a great variety of film forming polymers, even photoresist can be used as the coating layer. Fig. 2D shows a GO monolayer on a glass coverslip imaged with a PMMA layer doped with a red-emitting laser dye DCM. This suggests that the scope of "on-sheet" microfabrication of graphene based devices can be significantly broadened using FQM.

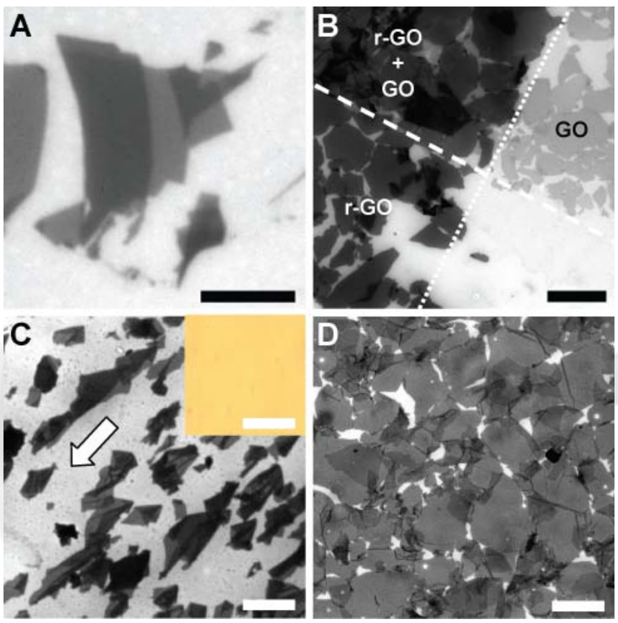

Fig. 2 FQM images of graphene based materials on various substrates. (A) Mechanically exfoliated graphene sheets on a SiO_2/Si substrate. (B) A cross-deposited GO/r-GO double layer on glass. (C) A spin-coated GO film on a polyester substrate. (D) FQM image of GO monolayer on glass acquire with a DCM/PMMA coating. In (A), scale bar=10 µm. In (B), inset of (C) and (D), scale bars= 50 µm. In (C), scale bar= 25 µm.

With FQM, it is also possible to directly observe graphene based sheets such as GO in solution, since GO becomes highly visible in a dye solution due to emission quenching. Fig. 3A is a bright-field image of an evaporating droplet of GO/fluorescein aqueous solution, in which GO sheets are barely visible. When switched to FQM mode (Fig. 3B), GO sheets were revealed. The real-time imaging capability thus enables the study on their dynamic solution behaviors, such as drifting (Fig. 3C) and pinning (Fig. 3D) during dewetting process of solution processed graphene based thin films.

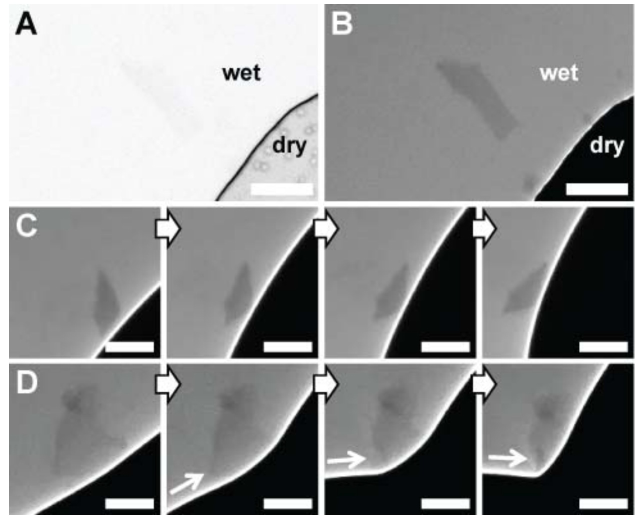

Fig. 3 FQM observation of GO sheets dispersed in dye solution. In contrast to (A) bright field image, GO sheets suspended solution becomes highly visible under (B) FQM, allowing in-situ, real-time observation of their dynamic solution behaviors such (C) drifting and (D) pinning during dewetting process. In (A) and (B), scale bars= 30 µm. In (C) and (D), scale bars= 15 µm.

Conclusions

Utilizing the strong fluorescence quenching effect, graphene based single atomic layer sheets can be visualized with a common fluorescence microscope by applying a dye doped polymer coating[5]. FQM can be used to image these 2D sheets on arbitrary substrates and even in solution. The highly versatile nature of FQM should make it a general imaging tool for high-throughput examination of graphene based materials[6].

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