

High-Contrast Visualization of Graphene Oxide on Dye-Sensitized Glass, Quartz, and Silicon by Fluorescence Quenching

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One of the keys to the successful discovery of graphene in 2004 was the possibility of detecting single graphene sheets deposited on a silicon substrate covered by a 300 nm thick oxide layer due to a weak interference-like contrast, which currently is the most practical way of identifying graphene sheets adsorbed on surfaces. Without this simple yet effective way to scan substrates for single- or multiple-layer sheets, graphene would have probably remained undiscovered.¹

This principle has been studied systematically and improved using various illumination setups.^{2–4} Under optimal conditions, the highest observable contrast of graphene on SiO_x is 0.12.² Very high contrast (0.8) can instead be obtained on Si₃N₄ substrates having a very precise Si₃N₄ thickness (67 nm) with the use of monochromatic illumination (550 nm).⁵

Graphene oxide (GO), although easier to produce and process than graphene, shares the same “visibility” problems.⁵ Since GO can be produced in large quantities and deposited as single layers on a wide variety of substrates, it is being intensively studied for applications in microelectronics, photovoltaics, and even biology.⁶ Here we demonstrate a novel approach for detecting and mapping GO on surfaces derivatized with an organic dye whose fluorescence is quenched in the presence of GO. In this way, visualization of GO sheets with high optical contrast (up to 0.78) can be easily accomplished on various substrates, including quartz and glass, without the need to use interference methods.

In this approach, a triethoxysilane fluorescent thiophene-based dye,^{7,8} *N*-(3-(triethoxysilyl)propyl 2,2':5',2'':5'',2'''-quaterthiophene-5-carboxamide (T4, Figure 1a), is covalently grafted onto the silicon dioxide, quartz, or glass surface through a microwave-prompted silanization reaction (i.e., reaction of Si–O–Et moieties with the OH groups of the SiO_x substrate).^{9,10} After T4 functionalization, intense green emission from the functionalized substrate is observed under UV excitation (Hg lamp, $\lambda_{\text{exc}} = 330\text{--}380$ nm), confirming the formation of a T4 layer.^{11,12} On the nanometric scale, the T4–SiO_x surface appears flat and uniform, as revealed by atomic force microscopy (AFM); the root-mean square roughness (R_{rms}) is comparable to that of unfunctionalized SiO_x (~0.2 nm as measured on $2 \times 2 \mu\text{m}^2$ areas). GO prepared by a modified Hummer method^{10,13} is then spin-coated onto the surface from a water solution. Through the use of thorough stirring instead of prolonged GO sonication, a large number of large, single GO sheets were formed on the surface, with lateral dimensions of up to 100 μm . The measured thickness of the GO monolayer was 1.1 ± 0.1 nm; similar values have previously been detected using AFM and are always somewhat larger than the real GO thickness, depending upon the measurement conditions and the presence of adsorbed water.¹⁴

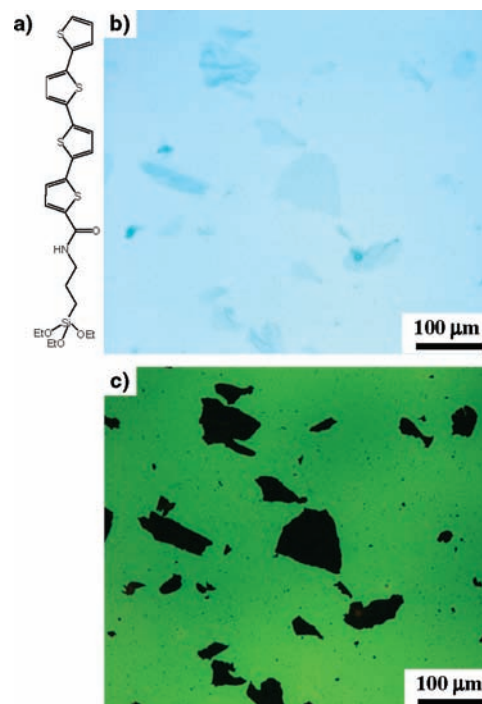


Figure 1. (a) Structure of the T4 molecule used for functionalization. (b) Optical microscopy image of GO sheets on T4-functionalized, 300 nm thick SiO_x. (c) Fluorescence image of the same area. The image has not been processed in any way to enhance contrast or luminosity.

Complementary X-ray diffraction (XRD) measurements performed on GO powders gave a more reliable value of 0.82 nm, in agreement with previous results.¹⁰ Topographical AFM images (Figure 2) show that most of the sheets are monolayer-thick, sometimes folding upon themselves, a behavior previously observed for GO adsorbed on neat SiO_x surfaces. Thus, both the morphology and apparent thickness of GO deposited on the T4 layer are comparable to those of GO on clean, bare SiO_x.

After deposition on the functionalized substrates, GO multilayers or folded single sheets were visible on the surface by optical microscopy (Figure 1b), albeit with low contrast.

Conversely, the fluorescence image of the same area ($\lambda_{\text{exc}} = 330\text{--}380$ nm, $\lambda_{\text{em}} = 487$ nm) displayed a green emission from the T4 layer. Remarkably, while the correspondence of many quenched areas of Figure 1c to the thicker GO deposits already visible in Figure 1b is straightforward, fluorescence imaging allows one to monitor smaller GO sheets that went undetected using normal light. Although graphene is a “zero-bandgap” semiconductor, a ~0.25 eV bandgap was measured in GO using scanning tunneling spectroscopy.¹⁵ The fluorescence quenching observed can be

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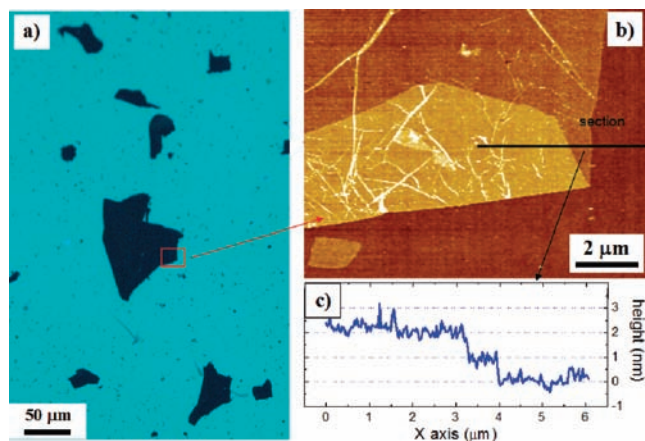


Figure 2. (a) Fluorescence image of a GO monolayer deposited on T4-functionalized, 300 nm thick SiO_x . (b) AFM image of the area indicated in (a), showing the GO sheet partially folded over itself (z range 30 nm). (c) Height profile taken across the black line in (b). The measured thickness of the GO sheet here is ~ 1 nm.

attributed to charge transfer from the T4 molecules to GO, as demonstrated by Raman spectroscopy and density functional theory calculations;¹⁶ comparison of fluorescence and AFM measurements recorded over the same areas (Figure 2) confirmed that even a single GO sheet can completely quench the fluorescence. The measurements shown in Figures 1 and 2 were performed using a 300 nm thick SiO_x layer (i.e., one possessing optimal conditions for graphene detection). The expected theoretical contrast^{2,5} for phase interference is either ~ 0.02 (considering an excitation wavelength of 330–380 nm) or below 0.05 (considering the T4 emission wavelength, which peaks at 487 nm). The contrast C measured¹⁰ in fluorescence images, however, reached values of 0.78 ± 0.01 (Table S1 in the Supporting Information), which is ~ 6 times the theoretical limit expected for light interference on 300 nm SiO_x .² The only equipment required to obtain this result was a low-pass optical filter, which was needed to exclude the excitation wavelength emitted by the lamp. The main advantage of this strategy is not only higher contrast but also the possibility of obtaining this result even on substrates other than 300 nm SiO_x without the need to change the illumination setup or optimize the substrate dielectric thickness. GO sheets deposited on 100 nm SiO_x , quartz, and glass substrates gave contrast values of 0.52, 0.20, and 0.07 which, although lower than in the previous case, are still more than sufficient for a clear visualization (see the Supporting Information).¹⁰

The contrast can be observed on so many different surfaces because it is due not to the mesoscopic structure of the substrate (which gives light interference) but rather to the “chemical” interaction between the GO and the T4 molecules on the molecular scale. T4-functionalized substrates possess high stability, and although slow quenching takes place under intense illumination, it is possible to visualize the GO sheets even after storing the samples for several days under ambient illumination in air. The contrast obtained in this work can be compared to the highest contrast attained for graphene and graphene oxide deposited on $\text{Si}_3\text{N}_4/\text{Si}$ substrates⁵ and is up to 6 times greater than the upper theoretical

limit attainable on SiO_x using only interference techniques.² Fluorescence and quenching of dyes in thin layers is already extensively employed as a highly sensitive tool in physics to measure orientation and dynamics of single molecules and in biology to measure subnanometer distances between living cells and SiO_x substrates.^{17–19} The results described here show that graphene visibility can be notably improved using this technique. More importantly, this approach is not limited to GO and SiO_x substrates and can in principle be applied to nonoxidized graphene as well as to the functionalization of various materials, allowing the visualization and study of graphene over a much wider range of surfaces than is currently possible. While the resolution attained by optical microscopy is limited by the wavelength of visible light (i.e., a few hundredths of nm), fluorescence emission of nano-objects and single molecules has been visualized using many non-diffraction-limited techniques,²⁰ so it would be possible in principle to study the fluorescence (or lack of fluorescence) of nanosized GO sheets. The approach presented here represents a simple strategy for studying the interactions between graphene and organic molecules with good control (thanks to the layer structure) of the molecule’s position relative to the graphene sheet.

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Supporting Information Available: Preparation of GO and T4-functionalized substrates, XRD patterns, UV–vis spectra, the contrast measurement formula, and fluorescence images of GO on different substrates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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