Detecting Graphene: new molecules for fluorescence imaging and dynamic sheet tracking

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Production of graphene via exfoliation of graphite flakes is one of the easiest and cheapest way to get it. Surfactants can be exploited to obtain "green" dispersions of graphene (G) in water media, and in particular non-ionic surfactants, like Pluronics, were demonstrated to yield particularly high fraction of exfoliated material[1]. However presence of the surfactants strongly affect the surface properties of graphene and this kind of chemical production is often associated to the uncertainty above exfoliation quality. Unfortunately there are very few techniques to characterize directly size and thickness in solution, like liquid-state Raman spectroscopy or Cryo-High Resolution Transmission Electron Microscopy(Cryo-TEM), but they can't assess the presence of surfactant on the top of graphene as far as describe the dynamic behavior carbon materials of the solution.

Based on new designed fluorescent surfactants, we report an easy, quick, innovative method to understand what's really happens inside of the solution as far as the real dynamic interaction between G-sheet/surfactants and G-sheet/ G-sheets. Exploiting the characteristics of the designed system, G-sheet/fluorescent surfactants we coupled Widefield Fluorescence Microscopy with a CCD camera to track graphene flakes motions and dynamics, going beyond the information provided by the study of the static system with fluorescence quenching microscopy (FQM) [2].Studying graphene Brownian motion permits to estimate some useful parameters like velocity and hydrodynamic volume to understand the dimension, motions and aggregation of 2D sheets. Our present results demonstrate that those fluorescent surfactants can be exploited to bring enormous adavantage for both characterization and design of new exfoliation pathways.

Fluorescent Pluronic® P123(**P**) surfactant was successfully synthesized with a new solvent-free reaction performed by reacting the pristine **P** with two isothiocyanate fluorophores: rhodamine B(**R**) or fluorescein(**F**). As shown in Figure 1, the fluorescein derivative, PF, and the rhodamine functionalized Pluronic, PR, were used to prepare water dispersions of graphene (G) by direct ultrasonication; slightly modifying the ultrasonication conditions reported by Guardia et. Al[3].The graphene aqueous suspensions G-P, G-PF and G-PR (Figure 1), were characterized during the exfoliation process by following PF and PR signals. Direct comparison of fluorescence anisotropy measurements, absorption and fluorescence spectra of the different samples allowed us to estimate the efficiency of adsorption of the fluorescent molecules onto graphene as well as the kind of interaction between the fluorescent moieties and the carbon structure. Direct HR-TEM image and diffraction pattern on sample G-P, G-PR and G-PF reveals the effective exfoliation, with average number of layers per flake N = 2-3.

Exploiting the obtained results with G-PF sample, we prepared a thin layer solution (0.12±0.01 mm) and observed it with an optical microscope in transmission mode, using a high magnification objective (100X). Fluorescence of the same thin layer of liquid sample G-PF with a wide-field excitation (λ_{exc}= 480nm), allowed us to observe and track individual carbon particle.

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In the end we obtained a fluorescent molecules, PF, that upon dyes excitation, permit to track graphene particles directly inside the solution. PF-fluorescence creates a visible contrast of optical intensity between background and the graphene sheets. This allows to perform particle tracking, Figure 2, for a quantitative and qualitative analysis of carbon nanomaterials. We used this approach to investigate the possible correlation between the size of the observed objects and graphene aggregates observed by TEM. Average diffusion coefficient k of the graphene particles was $k = 285 \pm 60 \ m^2 \bullet s^{-1}$. This value correspond to sheets of lateral 1D size ≈ 350 nm size in agreement with TEM measurements, that reported 1D size of $\approx 220 \pm 1$ nm. The synthesized fluorophores, as far as the synthetized systems, allowed to understand: (i) the interaction between graphene and fluorescent molecules,(ii) understand the actual function and distribution of surfactants during the exfoliation process,(iii) and exploit that results to solve the problem of graphene nanomaterials direct-imaging that those fluorescent surfactants. Based on low cost: surfactants, chromophores and instruments; this work is a tool that can be exploited for characterization of liquid graphene suspension both for industrial and laboratory production.
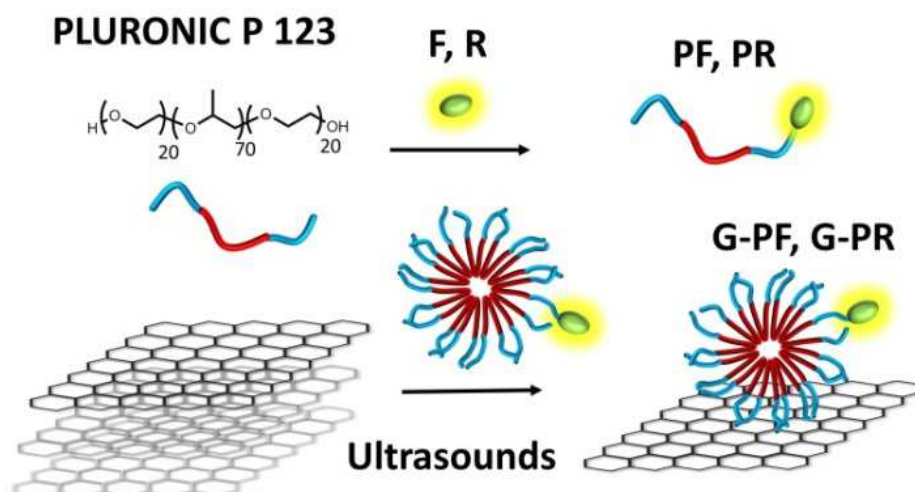

Figure 1: a) Top: reaction of the neutral surfactant Pluronic F 123 with either fluorescein (F) or rhodamine (R) isothiocianate. Bottom: Scheme of the exfoliation process.
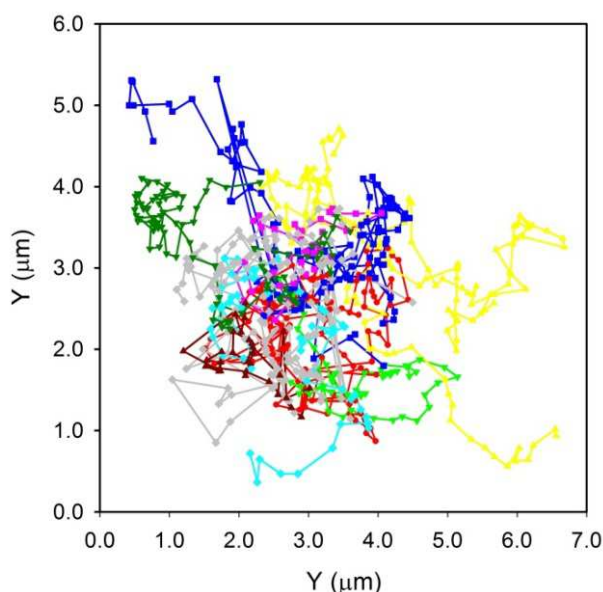

Figure 2 . Particle tracking: Brownian trajectories of graphene. Performed on G-PF system, with Fluorescence Wide field Microscopy.