Surface Functionalization of Graphene Studied by the in-situ Combination of μGISAXS and Electrical Measurement

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Graphene, a two-dimensional one-atom thick layer material, is considered as ideal material for high-sensitivity miniaturized electrical biosensor. One type of device structures is ion-sensitive field-effect transistors using graphene as channel material [1]. The operation principle is to monitor the change of transfer characteristics resulting from the change of the electrical properties of electrical double layer close to the graphene surface during binding of molecules. For real application, graphene biosensors should be able to sense a specific type of molecules of interest. In general, due to the presence of π electrons, the graphene surface has a rather high affinity to different biomolecules, resulting in poor specificity. In order to capture a specific type of biomolecules and block the others, graphene surfaces should be functionalized in a proper fashion. For DNA sensing as an example, this usually involves coating the graphene with a monolayer of small organic molecules as linkers followed by linkage of DNA probes [2-4].

From the fundamental viewpoint, it is of importance to probe the interaction of small molecules with graphene in real time. The main purpose of this joint work is to combine grazing incidence small angle scattering (GISAXS) technique with electrical measurement to investigate the deposition of DNA probes in liquid on graphene in the configuration of field effect transistor at the P03 beamline at the PETRA III synchrotron storage ring (Figure 1a). By the unique combination of the above-mentionend methods, we will finally investigate the surface functionalization of graphene by DNA probes *in operando*.

In this work, we have performed in-situ real time μGISAXS combined with electrical characteristic measurement at the P03/MiNaXS beamline [5] of PETRA III storage ring during the deposition of DNA probes in solution on graphene via high precision syringe pump system. A drop of DNA solution is deposited on a single-layer graphene on SiO_2/Si that is connected by two silver electrodes which are applied with 0.1 V and grounded, respectively. A Pt wire is in contact with the DNA solution drop used as gate electrode on which gate voltage will be swept from – 1 to 1 V repeatedly. This is a typical graphene based liquid-gated field effect transistor. The experiment setup is shown in Figure 1b, c. A microfocused x ray beam of 25x11 μm^2 with energy 18.3 KeV was employed and the detector is Pilatus 1M, Dectris. The experiment was carried out with the sample-to-detector distance 3836.26 mm, the incidence angle of 0.3° and the detector exposure period of 1 frame/s.

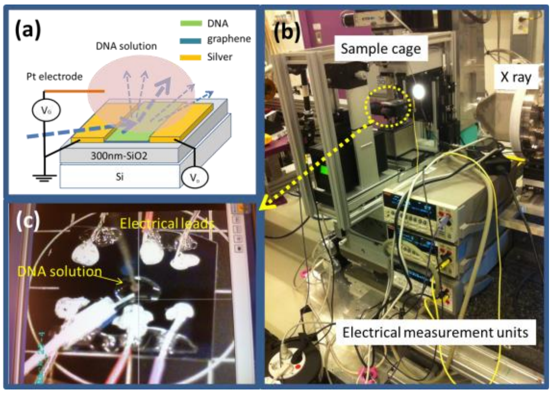

Figure 1. (a) a schematic of DNA solution trop applied on a graphene transistor measured in-situ by means of the combination of μGISAXS and electrical measurements, (b) a photo of the electrical measurement units equipped at the at the P03/MiNaXS beamline and (c) the photo of the sample in test

Figure 2 presents the results of the in-situ μGISAXS measurements during solution-phase deposition of DNA. Figure 2a is the out-of-plane cuts (along q_y) as a function of time where two lines are visible which correspond to the Yoneda peak of graphene and DNA layer, respectively. Figure 2b is one typical μGISAXS pattern recorded at a specific time during DNA deposition. In Figure 2c, the evolution of the transfer characteristics of the device during the deposition of the drop of DNA solution is presented. It shows that the substantial change in on/off current ratio when the solution drop is in contact with the graphene surface and subsequently drying. The correlation of the results of µGISAXS measurements to those of electrical measurement which shed light on the process of DNA deposition from solution and the influence on the electrical performance of graphene transistor.

In summary, we have successfully been able to follow the surface functionalization by deposition of DNA probes from solution on graphene via the combination of µGISAXS and electrical measurements. Further analysis is ongoing and will provide a deeper understanding of the DNA deposition on graphene.

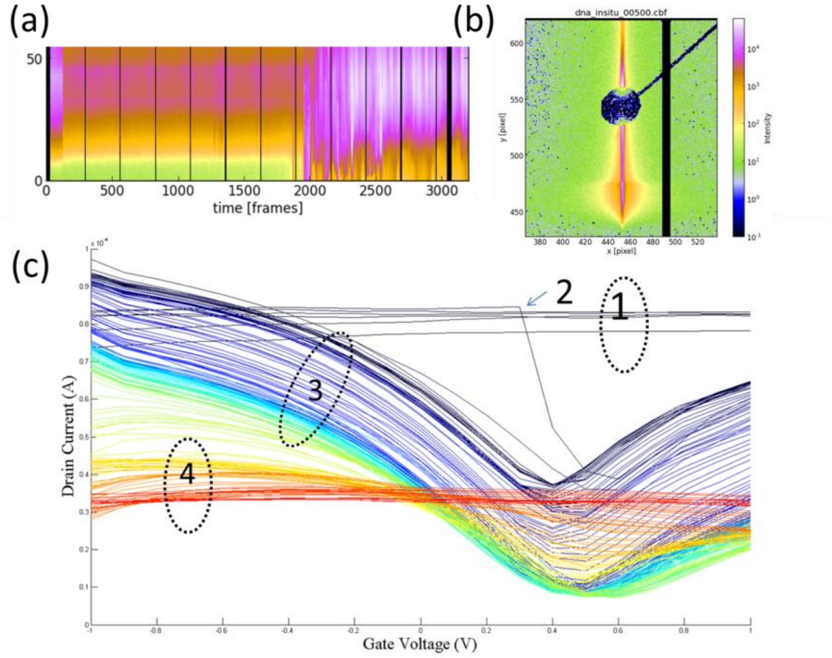

Figure 2. (a) Out-of-plane cuts along q_y of the DNA signal as a function of time cut from µGISAXS patterns of DNA deposition from solution, (b) a snapshot of a µGISAXS pattern and (c) transfer characteristics of graphene transistor (1) before, (2) at the moment when, (3) after the solution drop containing DNA probes contacts the graphene and (4) after drying of the drop.

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