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Effect of substrate and subphase conditions on the surface morphology of graphene oxide sheets prepared by Langmuir–Blodgett technique

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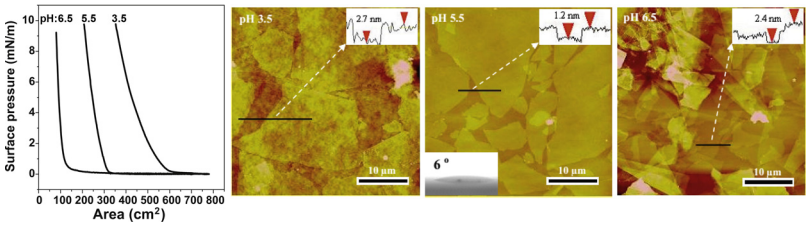
HIGHLIGHTS

- Langmuir monolayer characteristics of GO sheets are highly sensitive to subphase pH.
- Compressible Langmuir monolayers prone to morphological deformation during transfer.
- RCA-1 treatment of Si and SiO_2 essential for transfer of flat and adherent GO sheets.
- Microscopic inhomogeneities on Si critically influence the morphology of GO sheets.
- Morphology of GO sheets on SiO_2 is insensitive to subphase and transfer conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide (GO) sheets were transferred by Langmuir–Blodgett technique on Si and SiO_2/Si substrates. The surface pressure – area isotherms of 'amphiphilic' GO sheets at the air–water interface are found to be highly sensitive to subphase pH, which significantly affects their hydrophilicity and the interaction between the sheets. The surface morphology of GO sheets transferred under different subphase and transfer conditions has been studied. RCA-1 (NH_4OH:H_2O_2:H_2O – 1:1:2) treatment of Si is found to be necessary for the transfer of GO sheets. The deposition on RCA-1 treated Si, is also highly sensitive to the compressibility of the Langmuir monolayer. Thus, transfer of well defined, uniformly distributed and flat GO sheets on Si is possible only in a narrow window of process parameters, namely, subphase pH, target pressure and lifting speed. In contrast, the transfer behavior and morphology of GO sheets on RCA-1 treated SiO_2/Si is practically insensitive to changes in subphase pH, target pressure and lifting speed. This behavior is attributed to the uniformly strong hydrophilic character of SiO_2/Si surface, compared to that of Si. The different behavior of Si surface, even after RCA-1 treatment, is attributed to its microscopic chemical and topographical inhomogeneities.

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1. Introduction

Graphene oxide (GO) has recently been attracting attention as a novel material. This is because, its electrical properties can be modified by a variety of de-oxygenation processes to form reduced graphene oxide (RGO), which is considered to be an alternative to graphene for applications in nanoelectronics, photovoltaics and sensors [1–3]. GO sheets consist of a mixture of sp^2 and sp^3 hybridized carbon atoms, bonded with hydroxyl and epoxide groups on the basal plane, and ionizable carboxylic acid and phenolic groups at the edges [4–6]. The poly-aromatic islands of un-oxidized benzene rings on the basal plane impart hydrophobic character to GO sheets [4]. Owing to the presence of hydrophilic and ionizable carboxylic groups at the edges, GO sheets behave as amphiphilic 'molecules' and can be spread as a Langmuir monolayer at the air–water interface [7]. In a pioneering work [8], the amphiphilic nature of GO has been exploited to transfer GO sheets from air–water interface on to solid substrates by Langmuir–Blodgett (LB) technique. Thick films of GO sheets have also been obtained by several approaches, such as, drop casting [9], spin casting [10], dip coating [11], spray coating [12] and electrophoretic deposition [13]. Most of these approaches often yield agglomerates of GO and overlapping sheets with folds and wrinkles, formed during solvent evaporation [3,11,13]. In contrast, LB technique can be used to transfer GO sheets of controlled morphology on solid substrates [8,14–16]. LB technique has also been extended to deposit GO multilayers by sequential transfer of GO sheets [8]. LB transferred GO sheets, after subsequent reduction to RGO and O_2 plasma etching, have been used to obtain a graphene nanomesh, which has been utilized as a channel in field effect transistors [17].

There are limited studies on the surface pressure – area isotherms of GO sheets at the air–water interface and their transfer behavior under different subphase and LB transfer conditions. Imperiali et al. [18] have studied the stability and structure of GO sheets at the air–water interface after different number of cycles of compression and expansion. They have shown that GO sheets rearrange upon repeated compression, without any loss of material at the air–water interface, and display reversibility of wrinkle formation, like elastic membranes. Cote et al. [19] have shown that subphase pH has a significant influence on the hydrophilicity of GO sheets and hence, on their packing at the air–water interface and transfer to hydrophilic substrates. Wang et al. [20] have shown that the size of the transferred GO sheets is influenced by the pH of the spreading solution. Zheng et al. [16] have used different levels of centrifugation to control the size of GO monolayers dispersed in water–methanol mixture. They have shown that the density of GO sheets and wrinkle formation depend on transfer conditions, such as, target surface pressure and dipper speed. In a different approach, Szabo et al. [21] have used GO sheets dispersed in water as subphase and a spreading solution of octadecyl ester of rhodamine B (RhB18) in chloroform, to form a hybrid monolayer. They have observed that the architecture of the hybrid monolayer is controlled by subphase pH and concentration of GO in the subphase.

It is expected and known to certain extent that the subphase pH dependent hydrophilicity of GO [19] and the wettability of the substrate play significant roles in the transfer of GO sheets from the air–water interface to solid substrates. However, despite several reports, a complete understanding of the role of subphase pH and LB transfer conditions in determining the surface morphology of GO sheets transferred on technologically important substrates, such as Si and SiO_2, is lacking. It may be pertinent to note that different forms of GO, namely, sheets of different sizes, multilayers, graphitic particles and aggregates, having different levels of hydrophilicity are present in the GO dispersion. This work attempts to systematically analyze the effect of subphase pH, together with other LB transfer parameters, such as, target pressure and lifting speed, on the surface morphology of GO transferred on to Si and SiO_2 surfaces, with wettabilities modified by RCA-1 (NH_4OH:H_2O_2:H_2O – 1:1:2) treatment [22]. Further, it explores the relative importance of substrate wettability vis-à-vis, the subphase and LB transfer conditions and attempts to identify the processing conditions, under which, uniformly distributed, morphologically flat, wrinkle-free and adherent GO sheets can be transferred on Si as well as SiO_2 substrates. Our results show that GO sheets with morphological features as above, can be transferred on RCA-1 treated SiO_2 substrates having low contact angles (~5°) under a wide range of subphase pH and LB transfer conditions. In contrast, Si substrates having nearly the same contact angle require a stringent control of the process parameters, which is attributed to the presence of microscopic inhomogeneities on the surface of Si, even after RCA-1 treatment.

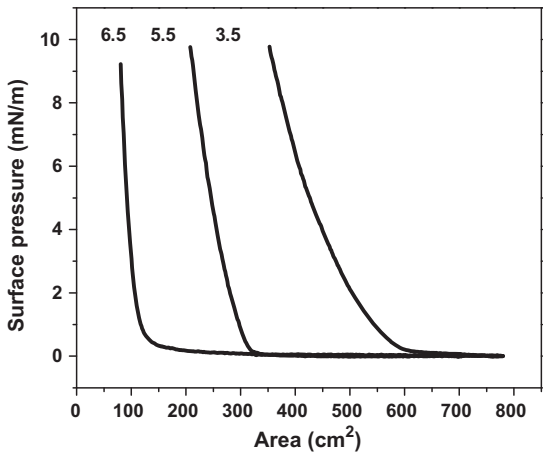

Fig. 1. Surface pressure – area isotherms of GO sheets at different subphase pH, as indicated in the figure.

2. Experimental details

GO was synthesized by a modified Hummers–Offeman's method [23], as described earlier [14]. The GO collected after exfoliation and centrifugation was dispersed in water–methanol mixture (1:5) to form a colloidal dispersion, which was used as spreading solution. Ultra-filtered and de-ionized water (Millipore, 18.2 MΩ cm) was used as subphase. The subphase pH was varied between 2 and 7 by adding dilute HCl/$NaHCO_3$ solution, as required. Concentration of GO in the spreading solution was maintained by monitoring the absorbance of the GO dispersion. For all LB deposition experiments, 20 ml of GO dispersion was spread on the subphase, and allowed to stabilize for 60 min before compression. The Langmuir monolayer thus formed, was compressed at a constant barrier speed of 5 mm/min. Silicon wafers, with and without thermally grown SiO_2 layer (~100 nm) were used as substrates. Si and SiO_2/Si substrates were initially cleaned with organic solvents and rinsed ultrasonically with de-ionized water. LB deposition was carried out on Si and SiO_2/Si substrates, with and without the RCA-1 treatment. GO sheets were transferred at target pressures, in the range of 1–30 mN/m. Owing to the hydrophilic nature of the substrates and the GO sheets, LB transfer took place only during the lifting of the substrate from the subphase. The lifting speed was varied in the range of 0.5–10 mm/min.

The surface morphology of GO sheets transferred on Si and SiO_2/Si substrates was studied with a Digital Instrument Veeco-Nanoscope IV Multimode scanning probe microscope in tapping mode. Micro-Raman spectroscopy was carried out with a Horiba Jobin Yvon HR800 confocal Raman microprobe, equipped with a 514 nm Ar^+ laser. The hydrophilicity of Si and SiO_2/Si substrates,