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Influence of graphene exfoliation on the properties of water-containing adlayers visualized by graphenes and scanning force microscopy

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ABSTRACT

Molecular adlayers on mica have been visualized previously by coating the sample with graphene and imaging it by scanning force microscopy. While it had been argued that this shows that ambient water on mica exhibits ice-like structures, recent apparently similar experiments indicate different behaviors. Here, we demonstrate that adhesive tapes, which are often used to mechanically exfoliate graphenes onto solid substrates, can lead to water-containing adlayers, which differ substantially from pure water layers. We exfoliated graphenes with the aid of different adhesive tapes and demonstrate that the results depend on the particular tape. Our results imply that structure and properties of confined water adlayers can be controlled by minor amounts of additives.

1. Introduction

Structure and properties of thin fluid films of molecular adsorbates on solid surfaces or in ultrathin pores are of broad scientific and technological importance [1–4]. On hydrophilic surfaces at ambient conditions, water is known to form a molecularly thin layer. Muscovite mica, a naturally occurring layered crystal, exhibits macroscopically large hydrophilic and atomically flat cleavage planes. It is therefore widely used as substrate for Scanning Force Microscopy (SFM). While the formation of a water meniscus between the SFM tip and the surface makes high resolution imaging of the adlayer challenging [5], it has been reported that graphene exfoliated on mica at ambient, coats the water adlayer, and makes it thereby possible to image the adlayer with high resolution SFM methods [6]. Graphene, a monolayer of carbon atoms covalently bound into a honeycomb lattice, has been demonstrated to be highly flexible to follow the topography of substrates with precision down to single molecules [7]. Moreover, graphene is also impermeable to small molecules, and thus, it not only replicates the topography but also conserves the film [8,9]. Therefore, coating with graphenes is being recognized to be an attractive way to investigate properties of confined molecular films [6,10–17].

There is, however, a certain discrepancy in the recent reports of the structure of the confined water film. The water layer has been argued to be ice like, as implied by the shape persistence of the water islands and their height of 3.7 ± 0.2 Å [6]. The flat islands were attributed to water molecules, since surface coverage was reported to correlate with the ambient humidity during sample preparation. Later, however, the correlation with the ambient humidity could not be verified [13]. Furthermore, flat islands of a similar height (~4 Å) have been reported for graphenes exfoliated on mica at very low humidity and therefore were not attributed to water molecules [18]. Moreover, the water layer confined between mica and graphene was argued to be fluid and to remain in equilibrium with the ambient water [12].

The exfoliation of graphenes is often carried out with adhesive tapes [6,19,20]. We noticed that the topographies of graphenes exfoliated onto mica surfaces with and without the aid of adhesive tapes differ substantially, as we will describe in the following. We attribute this to graphene contaminations originating from the adhesive tapes implying that the structure and properties of molecular layers confined under graphenes may vary depending on the particular brand of adhesive tape used. In order to test this, we exfoliated graphenes with the aid of two different adhesive tapes, which will be referred in the following as **1** (3M France Ltd., type "810") and **2** (Nitto Denko UK Ltd., type "SWT 10+"). The exfoliated graphenes were imaged at variable ambient humidities.

2. Materials and methods

Graphenes were mechanically exfoliated onto mica from highly oriented pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics) at ambient conditions either with or without the aid of adhesive tapes. The adhesive tape-free exfoliation method has been described previously [12]. The adhesive tape exfoliation was carried out under the same experimental conditions as the tape-free

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exfoliation. For that, adhesive tape is pressed against a HOPG crystal such that the top few layers become attached to the tape. The layers on the tape are cleaved further by folding the tape a few times. Then, the tape is pressed against freshly cleaved mica surface. Single layer graphenes have been detected via back-illuminated optical microscopy [21]. In order to verify the influence of relative humidity on graphene topography, the SFM imaging was done first under ambient condition; afterward, the humidity was reduced by continuous purging of the SFM chamber with dry nitrogen. After a certain delay, as indicated, humidity was increased to roughly 60% by purging the SFM chamber with dry nitrogen bubbling through water. SFM imaging was performed in tapping mode with Nanoscope IV Multimode (Bruker Corporation). Silicon cantilevers (Olympus Corporation) were used with typical resonance frequencies of 70 kHz and 300 kHz and spring constants of 2 N/m and 42 N/m, types OMCL-AC240TSG-W2 and OMCL-AC160TSG-W2, respectively. For the height analyses, the piezo was calibrated assuming the step height between the single and the double layer graphene to be 0.34 nm. Indicated errors of heights are the standard deviations. The relative humidities (RH) and the temperatures were measured with testo 635 of Testo GmbH equipped with a capacitive sensor. The sensor was located in a close proximity to SFM head. The calibration fidelity of the sensor is ±2.5% RH in the addressed RH range, as provided by the manufacturing company. RH values indicated in the text are the displayed values.

3. Results

More than twenty samples have been prepared *without* the aid of adhesive tape. The results for all samples are qualitatively similar. When prepared and imaged under ambient humidities between roughly 30% and 70% RH [12], the surfaces of graphenes are for the most part flat, i.e., free of flat islands typical for graphenes exfoliated with the aid of adhesive tapes (see below) (Fig. 1a and b). Occasional defects are attributed to folds, cracks, and other structural defects, which occur typically on graphenes prepared by mechanical exfoliation. The mica surface is often covered by a scarce number of protrusions, which were previously attributed to potassium carbonate crystals forming on mica surface at ambient [22]. The apparent height of single layer graphenes on mica varied in the range of −1.3 to 1.5 nm, being sometimes indeed negative; this has been attributed to different tip-surface interactions on bare mica and graphene covered areas [12]. Upon drying of the SFM chamber, fractal depressions (Supporting information) grew in the graphene. They were attributed previously to the dewetting of a monomolecular layer of water molecules confined between mica and graphene [12]. The increase in the humidity to 60% erased the depressions.

Two samples were prepared with the aid of adhesive tape **1**. The results for both samples were qualitatively similar. For one sample, the number of graphene layers was optically quantified, which we describe in the following. A few layer graphene flake was exfoliated onto a mica surface at ambient conditions (RH = 41%, T = 23 °C), and the SFM topography images are shown in Fig. 2. One can recognize a large flat island with the height of 4.3 ± 0.2 Å within the single layer graphene. Drying of the SFM chamber caused growth of depressions of a rather compact shape within flat elevated island and fractal like depressions in the underlying graphene planes (Fig. 2b and c) readily after 20 min of drying. The depth of a few compact depressions was 3.6 ± 0.3 Å with the lateral size larger than 50 nm, i.e., larger than the SFM tip radius. Comparison of the images made before and after drying revealed furthermore receding of the islands' edges. The receding edges left almost no traces except a few small protrusions, i.e., receding edge maintained the height of the island. The growth of the depressions slowed down such that we could not detect any further growth after two hours of continuous purging of the SFM chamber with dry nitrogen (not shown). Increase in humidity to 60% erased both compact and fractal like depressions (Fig. 2d).

Another two samples were prepared with the aid of adhesive tape **2**. Again, the results for both samples were qualitatively similar; however, the number of graphene layers was optically quantified for only one sample which we describe in the following. Fig. 3 displays SFM topography images of few layer graphene flakes exfoliated with the aid of adhesive tape **2** onto a mica surface at ambient conditions (RH = 39%, T = 24 °C). Similarly to tape **1**, the graphenes exhibit flat islands with a height of 5.1 ± 0.6 Å. In addition to flat islands, one can recognize a number of structures with variable shapes from image to image (Supporting information) and strong contrast in the phase image (Fig. 3b). Therefore, we attributed them to molecular adsorbates on top of graphene and did not analyze them any further. Furthermore, one can recognize a number of smaller protrusions of a similar height. Purging the SFM chamber with dry nitrogen for about one hour caused growth of a small number of compact depressions within the flat islands (Fig. 3c). Unlike for samples prepared with the adhesive tape **1**, we could not detect growth of any depressions within the underlying graphene planes.

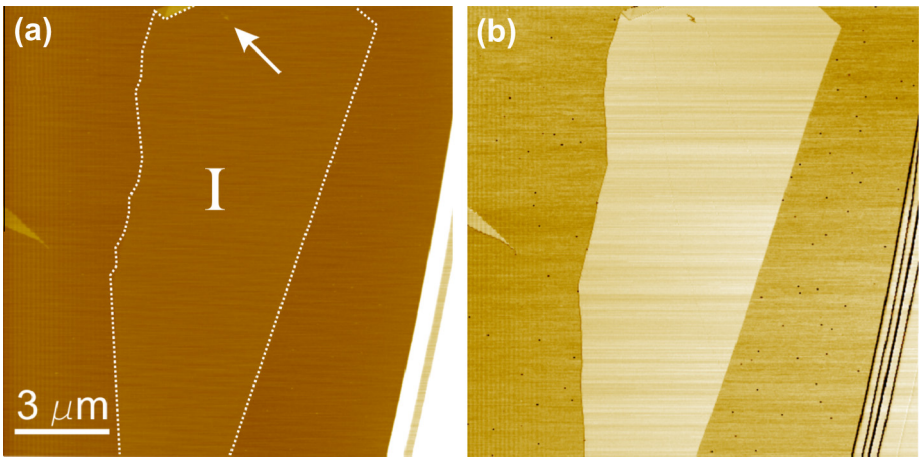

Fig. 1. SFM (a) topography and (b) phase images taken simultaneously on a graphene exfoliated onto a mica surface *without* the aid of adhesive tape. The area recognized to be single layer graphene is indicated with **I** and outlined with a white dashed line. The single layer graphene is mostly flat, but a defect in the upper part of the image is indicated with an arrow. The faint periodic oblique lines are instrumental noise. The apparent height of the graphene on mica is ~0.5 Å (see also main text). The mica surface is covered by small and scarce protrusions visible in both topography and phase images.