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Re-organized graphene nanoplatelet thin films achieved by a two-step hydraulic method

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ABSTRACT

Film deposition of graphene nanoplatelets (GNPs) from dispersion via casting and printing approaches features cost- and material-efficiency, however, it usually suffers from poor uniformity, rough surface and loose flake stacking due to adverse effect of hydraulic force. Here, a simple two-step method exploiting hydraulic force is presented to readily deliver GNP films of improved quality from an aqueous dispersion. While as-deposited GNP films exhibit the aforementioned film defects, the hydraulic force in the subsequent step constituting soaking in water and drying leads to an efficient re-organization of the individual GNPs in the films. The majority of GNPs thus are oriented horizontally and closely stacked. As a result, densified, smoothened and homogenized GNP thin films can be readily achieved. The GNP re-organization reduces resistivity from $> 1\,\Omega\,cm$ to $10^{-2}\,\Omega\,cm$. The method developed is universally applicable to solution-phase film deposition of 2D materials.

1. Introduction

Graphene, a two-dimensional lattice of carbon with a thickness of only one single atom has attracted considerable attention in recent years due to the unique electronic, mechanical and thermal properties [1–5]. Graphene can be obtained using graphite as raw material by means of micromechanical cleavage [6,7], chemical oxidation and reduction resulting in reduced graphene oxide (RGO) [8,9] and liquid-phase exfoliation procedure giving rise to pristine few-layer graphene nanoplatelets (GNPs) [10]. The liquid-phase exfoliation employs physical means, e.g., ultrasonication [11] and shear-exfoliation technique [12,13]. The exfoliated GNPs can form stable colloidal dispersion with the aid of surfactants, polymers [11–13] and salts [14,15]. GNPs are normally studied and applied in the form of GNP dispersions. The availability of GNP dispersions enables cost- and material-efficient thin film deposition on a variety of substrates under ambient condition. For example, spraying and printing techniques (inkjet printing, screen printing, gravure printing, etc.) can be readily applied in the areas associated with printed electronics, [13,16–19] surface coatings against corrosion, [20] conductive electrodes for energy application [21] and chemical barriers in environmental protection [22,23].

Uniformity over large area and a good control over structural properties are prerequisite for GNP thin films in real applications. For the application as conductive coatings and chemical barriers, it is an additional necessity that nearly all individual GNPs in a film are horizontally oriented, closely stacked and densely packed in order to maximize the electrical conductivity and the barrier performance towards small molecules. However, exploiting GNP dispersion for liquid-phase deposition poses many challenges in the formation of high quality GNP films [24–29]. The reported GNP films normally were carried out by depositing GNP dispersion followed by drying at elevated specific temperature. Likely due to the coffee ring effect during evaporation of the liquid, the GNP films usually show rather poor uniformity [26–28]. In addition, it is expected that fluid dynamics during solvent evaporation likely leads to uncontrolled and complicated orientation, stacking manner and interconnection of the GNPs in a film, which can influence the properties of as-deposited GNP films to a large degree. As the structure of an as-deposited GNP film is sensitive to the solution-phase processing condition, large variations from batch to batch and sample to sample are a common observation. Under this context, methods for deposition of GNP and other 2D materials from dispersions with controllable structures are highly desired.

In order to effectively remedy the defective aspects of GNP thin films directly deposited from dispersions, a simple two-step deposition method is presented, as briefly illustrated in Fig. 1. The first step (*step* 1) constitutes drop-casting of an aqueous GNP dispersion on a glass (Fig. 1(a)) followed by a baking process as conventionally utilized in many previous reports [24–29]. In principle, inkjet printing of 2D

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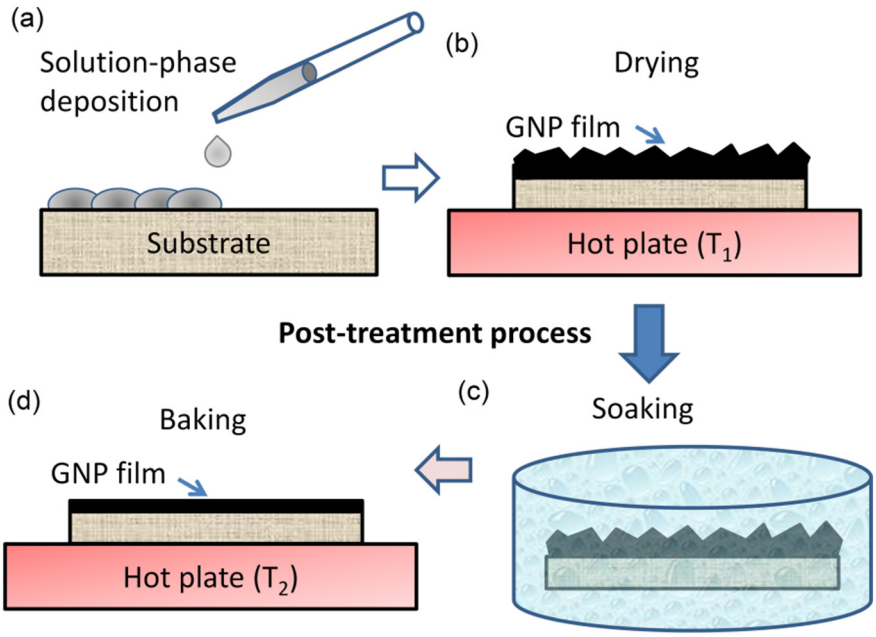

Fig. 1. Schematic illustration of the two-step GNP film deposition procedure from aqueous dispersion, constituting *step* 1 including (a) drop casting, (2) drying at T_1, and *step* 2, including (c) soaking in DI water and (d) drying at T_2, for film re-organization.

materials in principle is similar with drop-casting. As shown below, this step results in GNP thin films of poor uniformity and rough surface (Fig. 1(b)). The subsequent step (*step* 2) involves soaking of the GNP films in deionized (DI) water (Fig. 1(c)) followed by a heat treatment (Fig. 1(d)). In *step* 2, hydraulic force is in action during the evaporation leading to an efficient re-organization of the individual GNPs within the films. As a result, the GNP thin films are significantly densified, smoothened and homogenized. The experimental results are highly reproducible, which is useful in real applications of GNPs. The method provided in this work can be applied to solution-phase film deposition of any kind of 2D materials.

2. Experimental section

The aqueous GNP dispersions with (Hydroxypropyl) methyl cellulose (HMC) as stabilizer were produced according to our procedure reported earlier [13,19]. By means of Raman measurement (data not shown), the majority of the GNPs used in this work have 2 to 3 layers. As *step* 1, the GNP thin films were deposited by drop-casting at 60 °C on glass placed on a hot plate (Fig. 1(a)). Then the substrate temperature was increased to 100 °C to dry the samples. Subsequently, the films were further dried at elevated temperatures, T_1 = either 200 or 300 °C, for 1 h (Fig. 1(b)). *Step* 2 constitutes a soaking of the GNP thin films in DI water for 0.5 h (Fig. 1(c)) and annealing typically at temperature T_2 = 200 or 300 °C for 1 h (Fig. 1(d)). The annealing was conducted by placing the samples on a hotplate when the set temperature was reached. After the set duration, they kept staying on the hotplate which power was shut off. Two to three samples were prepared under each condition. Electrical and thickness measurements were performed by the standard 4-probe technique (CMT-SR2000N Automatic Four-Point Probe) and probe profile meter (Bruker/Veeco Dektak 150 Stylus Profiler) with 13 μm in radius of the probe, respectively, on 3 to 6 spots on each sample. The stylus force was set 2 mg in order to minimize any destruction of the sample surface. The structural properties were determined by scanning electron microscopy (SEM, Zeiss 1530) and x-ray diffractometry (XRD, Siemens D5000). The GNPs and the polymer stabilizer were characterized by resonant Renishaw Raman spectroscopy with laser wavelength of 532 nm.

3. Results and discussion

The GNP thin films resulting from *step* 1, i.e., deposited from the aqueous GNP dispersions and baked at T_1, are challenged by a rather rough surface and porous feature, as revealed in the top-view SEM images (Fig. 2(a) and (b)). The application of *step* 2, i.e., soaking in water and baking at T_2 = 300 °C, leads to several distinct changes in surface morphology (Fig. 2(c) to (h)). First, the surface is flattened, as revealed in Fig. 2(d) and (e); second, above the surface sharp and narrow GNP "great walls" of ~200 nm in width are grown (Fig. 2(c), (d), (f), (g) and (h)); third, it appears that the GNPs are more horizontally oriented with less porous feature, as the image in Fig. 2(e) is compared to that in Fig. 2(b), which will be confirmed by XRD analysis later. The SEM images also show that the size of the GNPs is on the order of hundred nanometers. Our Raman analysis revealed that the majority of the GNPs consist of 2 to 3 monolayers (data not shown).

In order to characterize the changes in film thickness, uniformity and roughness, the probe starts to scan from the substrate and moves far inside the GNP film in the probe-profile measurement. As shown in Fig. 3(a), the profile curve goes up and down in a rather large degree of variation, showing that the GNP films of *step* 1 generally are very rough with the arithmetic average roughness of ~2 μm. In addition, coffee ring effect is observed as the films typically are thicker towards the edge. This is a typical unwanted feature of solution-phase deposited thin films of any kind which should be avoided. When looking more closely, one can find that the film around the edge is more porous than inside. By measuring the height far inside the films, the average thickness of the thin films prepared in this work is 2.1 ± 0.5 μm. For this specific film, the thickness is around 3 μm. After *step* 2, distinguishing changes are observed. First, the average thickness has shrunk dramatically. The final thickness of the studied films falls in to 0.54 ± 0.07 μm. Second, the films are substantially flattened as the roughness is reduced to ~0.15 μm. Third, more uniform films are obtained as the coffee ring effect is suppressed. It is observed that profile peaks of height from 100 to 200 nm are present, which most likely correspond to the height of the GNP walls as shown in Fig. 2. It shall be mentioned that the results are highly reproducible from sample to sample and batch to batch prepared at different times. The dramatic reduction in film thickness reveals that the GNP films after *step* 2 are