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Water front recession and the formation of various types of wrinkles in dried graphene oxide droplets

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ABSTRACT

We systematically investigate the spontaneous formation of various types of wrinkle patterns in dried GO droplets using different drying conditions including temperature, GO concentration, and ionic concentration. A coffee-ring effect occurs in biphasic dispersions with low GO concentration, which is suppressed in high-concentration nematic phases. In dried nematic GO droplets, more than five different wrinkle patterns, composed of two types of wrinkle lines parallel and perpendicular to the direction of water recession, are spontaneously produced depending on the drying conditions. The wrinkle patterns are dependent on the recession behavior of the water front and interparticle friction, both of which influence the shape and density of the wrinkles. The receding water front flattens the GO sheets on a flat substrate from the edge to the center of the droplet, causing an anisotropic compressive force on the GO sheets that orders the wrinkle pattern. Interparticle friction, which is enhanced by increasing either the GO or the ionic concentration, increases the wrinkle density and disturbs the order of the wrinkle lines.

1. Introduction

Spontaneous assembly of nano- or microparticles has long been of interest to both the academic and industrial sectors [1,2]. Useful self-assembly results have been reported in various fields, including DNA manipulation in biology [3], photonic crystalline particle assembly in colloids (nanofabrication) [2], and knotted particles in nematic fields [4]. One simple approach is to evaporate the volatile solvent from a colloidal solution. The process of solvent evaporation imparts unique effects on the dispersed particles, such as continuously increasing concentration, solvent flow, and anisotropic tensional stress. These effects are likely to produce fascinating surface morphologies and structures. Various evaporation methods to control nanoparticle assemblies and surface morphologies have been developed, such as sphere-on-flat geometry [5], dip-coating substrates [6], Benard-Marangoni convection [7], and receding meniscus [8].

Drying an aqueous graphene oxide (GO) dispersion is a well-known, facile method to fabricate GO papers or wires, and these can be used to obtain conductive reduced GO papers through chemical and physical reduction methods [9–12]. During the drying process, which is commonly used in solution processes [13], wrinkles usually appear in individual GO particles or in groups of GO assemblies [12,14,15]. Wrinkles and packed structures in dried GO films are desirable in various potential applications such as supercapacitors using vertically aligned GO assemblies and conductive papers [14].

Recently, Luo et al. reported the formation of macroscopic wrinkles by drying GO droplets [16]. They reported several interesting findings: i) the coffee-ring effect was suppressed during the drying process of GO droplets; ii) under ambient drying conditions, the depinning effect promoted an orthoradial compression of nematic GO alignment, resulting in wrinkle patterns with radial spikes; and iii) the form of a preexisting deformation in the alignment of a GO liquid crystal (LC) determined the wrinkle shape after drying. Based on this model, they produced radial spike and spider-web wrinkle patterns by predesigning the deformation patterns of GO LC alignments with radial band and circular band defects, respectively. Although the wrinkle formation mechanism has been intensively studied for various systems [15,17–20], the wrinkle structures of GO films are less explored.

In this study, we report and classify various types of macroscopic and microscopic wrinkle patterns. These patterns are spontaneously formed under various drying conditions, including temperature, and GO and ionic concentration. We analyze the wrinkle formation procedure near the dewetting boundary of a

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droplet, clarifying the compression stress near the dewetting boundary and the resultant radial and concentric wrinkle formations. The speed and shape of the waterfront and the frictional interaction between particles play an important role in determining the shape and density of the wrinkles.

2. Experimental

We prepared GO samples using a typical Hummers method, by following the procedure described in our recent publications [10,21]. Graphite powder (200 mesh, purity 98%) and all chemicals were purchased from Sigma–Aldrich Ltd (Seoul, Korea). Residual salts were removed by repeatedly centrifuging the sample (15 times) [22]. The mean thickness and diameter of the GO particles were measured using scanning electron microscopy (SEM, JSM-7500F, Joel Ltd., Japan) and atomic force microscopy (AFM, SPA-300HV, Seiko Instruments Inc., Japan) [22]. The average diameter of the GO flakes was 1.9 ± 1.7 μm, respectively, and the thickness was approximately 1 nm. The phase transition concentrations from isotropic to biphasic and from biphasic to nematic were 0.17 and 0.6 wt%, respectively, as determined via observation using birefringence microscopy [23]. Four different concentrations of GO dispersions were used: three nematic dispersions at 1, 2 and 4 wt%, and a biphasic dispersion at 0.4 wt%.

In order to investigate the effect of ions in the GO dispersions and wrinkle formation, we added different types of ions, i.e. NaCl, HCl, and NaOH, to the GO dispersions [24]. However, NaCl and NaOH crystallized and produced salt residues after drying, interfering with the identification of the wrinkles, and inducing an extrinsic effect on wrinkle formation (see Supplementary Fig. S1). Hence, we chose HCl ranging in concentration from 0 to 0.07 M, where the molarity denotes the HCl concentration in the final GO dispersion after mixing.

A GO droplet was dried under ambient conditions at 25 °C and 55% relative humidity. A BX53 microscope (Olympus, Japan) with a polarized optical mode and both bright and dark field reflection modes was used for droplet observation. The vertical profile of the wrinkles was measured using a stylus profiler, Alpha Step D-600 (KLA-Tencor Corp., USA). A CCD camera (CMLN-13S2M-CS, Pointgrey Co., USA) recorded the wrinkle formation process.

3. Results and discussion

3.1. Macroscopic wrinkles in dried GO droplets

GO droplets (5–10 μL) with different GO and HCl concentrations were deposited on a glass substrate, and dried at different temperatures. We did not intend to induce any GO alignment or deformation in the droplets, and thus, all droplets were dried as deposited. The details of the wrinkle patterns differed from one droplet to another, but the overall shape could be categorized as one of several types, as shown in Fig. 1. The types of the wrinkle patterns were obtained reproducibly by choosing the corresponding drying conditions (see Supplementary Fig. S2 for further information about reproducibility). The images shown in Fig. 1a–g displays the typical wrinkle patterns in dried droplets; the photos were taken using a bright field reflective microscope, and some images (a, d, and e) were obtained by stitching multiple micrographs together owing to their large size.

The coffee-ring effect was predominantly observed in the biphasic droplet with low GO concentration (0.4 wt%, 25 °C) [25], as shown in Fig. 1a. The water droplet boundary was pinned on the edge by the first deposit of GO. Thereafter, outward capillary flow carried the GO sheets from the interior of the droplet to the edge, giving rise to a thick ring pattern with dense wrinkles on the edge [25]. As drying progressed, the GO concentration within the droplet increased due to water evaporation. The higher GO concentration hindered both capillary flow and GO drift, depinning the droplet edge. GO particles in the center of the drop that had not drifted toward the edge created a significant amount of wrinkles upon drying [16]. Hence, a doughnut-shaped low-density wrinkle area was formed in the middle region. As either drying temperature or GO concentration increased, the pinning and GO drift were weakened and the density of wrinkles became more uniform over the entire area of the droplet, as shown in Fig. 1b. Thus, the coffee-ring effect, a typical phenomenon in colloids, can occur in aqueous GO dispersions as well, albeit to a weaker extent than typically seen with colloids. GO sheets are amphiphilic and are likely to move to the air–water interface during evaporation. When the amphiphilic GO sheets cover the surface of the droplet [26,27], they can decrease the solvent evaporation rate and the condensation of GO sheets on surface can suppress the coffee-ring effect. Hence, the coffee-ring pattern and donut-shaped wrinkle-free ring form only at very low GO concentrations.

In nematic droplets of high GO concentration, shown in Fig. 1b–f, the wrinkle lines filled the entire area due to a suppressed pinning effect. The wrinkle patterns varied greatly. The droplets in Fig. 1b–d had radial striations with varying thickness and shapes. Fine radial wrinkles filled the entire area of the 1 wt% GO droplet, dried at 25 °C (Fig. 1b), and thick spider web-like wrinkles formed in the center of the 4 wt% droplet dried at 80 °C (Fig. 1c). A fully grown spider web pattern was obtained by adding a small quantity of HCl ions to the solution (Fig. 1d). Luo et al. reported that in order to produce such a pattern, a circular band deformation with a single integer disclination in the GO alignment should exist before drying [16]. However, in our case, the spider web pattern developed spontaneously using a high GO concentration and high drying temperature, without predetermining GO alignment deformation.

The droplets in Fig. 1e–g shows randomly connected network patterns over the entire area. The density of this random network of wrinkles depends on the GO concentration, as can be seen by comparing Fig. 1e and f, in which HCl was added to induce a random network of wrinkles. A pattern similar to that in Fig. 1e was obtained in an aged GO droplet, stored for two weeks (Fig. 1g). It is known that the GO particles undergo C–C bond cleavage reaction accompanying H^+ ionic generation [28]. The increased concentration of H^+ ions resulted in a network-like wrinkle pattern in the aged GO dispersion. Fig. 1h shows polarized optical microscopy (POM) images for the radial pattern in Fig. 1b and the random network wrinkle pattern in Fig. 1g. The radial birefringent wrinkle lines at the top contrast sharply with the irregular speckled birefringent patterns at the bottom.

Thus, the shape, width, and density of the macroscopic wrinkles in dried GO droplets depend on the GO concentration, drying temperature, and ionic concentration; in particular, striation wrinkles predominantly appeared in pure GO droplets, and random wrinkles were predominantly created in GO droplets containing ions.

3.2. Microscopic wrinkles in dried GO droplets

Observation using microscopy revealed the details of the microscopic wrinkle structures. The microscopic wrinkle shapes fall into several categories, as shown in the images in Fig. 2a–2f, in which the top and bottom images were respectively taken by dark field- and bright field-reflective microscopy. In the microscopy images, the horizontal and vertical directions correspond to the radial and concentric directions of the droplets, respectively. The surface vertical profiles of these wrinkles were measured by scanning the samples in the concentric direction (vertical direction