



# Ionic interactions to tune mechanical and electrical properties of hydrated liquid crystal graphene oxide films



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## HIGHLIGHTS

- Free standing LCGO films were prepared via using LCGO dispersions treated with hygroscopic salts.
- Treatment of LCGO free standing films with a range of chloride salts enhanced mechanical and electrical properties simultaneously.
- Modified free standing LCGO films remained robust and stable under both dry and aqueous conditions.

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## ABSTRACT

Considerable improvements have been obtained in physical and mechanical properties of free standing liquid crystal graphene oxide (LCGO) films in their hydrated state, by modification of LCGO dispersions with a low quantity of chloride salts. Addition of salts to LCGO dispersions result in an increase of the storage and loss moduli and viscosity through the interaction between cations and functional groups of LCGO, with the magnitude of increase being dependent upon the concentration of the salt added. A viscosity increase of between 30× and 300× (depending on the salt type) is recorded when salt is added at a concentration as low as 80 mM while storage and loss moduli increase up to 23× and 29×, respectively. Free standing films made from the salt treated LCGO dispersions contained up to 26% water in their structure and were observed to have significantly improved mechanical (2× to 5× increase) and electrical properties (decreased surface resistance up to approximately 670×) compared to free standing films prepared without chloride salts. The influence of the salts on properties of LCGO dispersions and their hydrated free standing films is postulated as a complex interplay of many factors such as the size of cations, the valency of positive charge of the cations, ratio of charge and cations size, as well as the hygroscopic nature of the salts.

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## 1. Introduction

Graphene has opened new pathways for developing a wide range of novel functional materials [1]. Due to its extraordinary mechanical, electronic and thermal properties, it has been used in various applications, including field effect transistors, sensors, transparent electrodes, batteries, supercapacitors, optoelectronics,

biodevices, tissue engineering, and drug delivery systems [2–12].

Graphite, a planar structure made of multi-layered graphene sheets, is the main source of processable graphene derivatives such as graphene oxide (GO). GO is a unique unconventional soft material [13], which is one of the most scalable derivatives of graphene. It is a monolayer material consisting of a hydrophilic graphenic sheet bearing oxygen functional groups on its basal plane and edges [14].

Through the process of oxidation, different functional groups form on the graphenic sheets, which results in their exfoliation and render the individual sheets dispersible in polar solvents [4,15,16]. Large GO sheets exhibit fascinating properties such as the ability

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to form liquid crystalline dispersions (LCGO). LCGO dispersions can improve the processability and induce order in the resulting composite materials at atomic levels [17,18]. LCGO can be used to construct high strength, highly conducting, self-assembled layer-by-layer composites after reduction [18,19], and to make high surface area electrodes in energy storage applications [20,21]. The ability to produce LCGO in large scale and fabricate it into various functional structures, in a cost effective manner, is crucial for enabling its potential applications [22–24]. In this regard, LCGO obtained by chemical exfoliation of natural graphite has a great potential in large-scale production of graphene-based functional architectures. The properties of LCGO dispersion permits using scalable techniques such as wet-spinning, printing and coating with exceptionally low production costs. However, the development of large-area graphene based free standing films using LCGO or GO with high mechanical properties, flexibility, stability in water and conductivity, is still an ongoing challenge.

The development of free standing (FS) films based on GO and/or LCGO have been achieved using a variety of techniques such as solvent-casting and filtration [25]. Utilizing these one-step fabrication approaches to make FS films is very appealing due to their low processing cost, and can have high potentials for bulk production of graphene film for numerous applications. Although a variety of substrates such as indium tin oxide (ITO), polyethylene terephthalate (PET), glass slide, and thin copper films have been used to develop FS-GO films, none of them resulted in a film with appropriate mechanical properties, especially when in a wet environment [25,26]. Furthermore, films made of large sized graphene sheets break easily during transfer from the casting substrate onto the target substrate via lift-off techniques [25,27]. Hence, there are still critical needs for simple, environmentally friendly, and cost-effective approaches that are scalable for preparation of bulk quantities of high fidelity FS LCGO films with robust mechanical performance.

Hydrated GO films made by filtration of GO dispersions have been reported before with mechanical properties resembling those of GO films [28]. Whilst there are published reports on the chemical interaction of divalent cations on GO paper [25], little investigation has been performed to study the effect of mono and divalent salts on the mechanical and electrical properties of FS GO-based structures in their hydrated state. Herein, we reveal the gelation behaviour of LCGO dispersion with significant enhancements in the mechanical properties and electrical conductivity of resulting FS-LCGO films upon modification with low quantities of chloride salt of monovalent alkali metals ( $\text{Na}^+$ ,  $\text{K}^+$ ) and divalent alkaline earth metals ( $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ). Salt treated LCGO dispersions and films are referred to as m-LCGO, where LCGO represents liquid crystal graphene oxide and m is to highlight modification by chloride salts. These observations can be described in terms of the interactions between the functional groups of the LCGO sheets and the metals ions [26,29] and also could be interpreted by the salts physical properties such as ions size and the valency of positive charge of the cations, ratio of charge and cations size and/or hygroscopicity nature that influences the ability to taken up and retained moisture [22,30–33].

## 2. Materials and methods

### 2.1. Materials

Expandable graphite used as the precursor for synthesizing ultra-large GO sheets was obtained from Asbury Carbon (3772). Sodium chloride (NaCl) was obtained from Aladdin-reagent. Potassium chloride (KCl), calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) and magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) were purchased from Sigma-

Aldrich and used without further purification. All chemicals were analytical grade and their solutions were prepared using Milli-Q water (18.2 MOhms) (Nanopure water, Barnstead). LCGO dispersions were prepared following the process outlined previously [34]. Ionic modified liquid crystal graphene oxide films (here after referred to as m-LCGO hydrogel films) were prepared by adding required amounts of salt solution (e.g. NaCl, KCl,  $\text{MgCl}_2$  or  $\text{CaCl}_2$ ) to (15 ml) of the ( $7.1 \text{ mg ml}^{-1}$ ) LCGO aqueous dispersion. Milli-Q water was added where required to maintain the final concentration of LCGO at  $3 \text{ mg ml}^{-1}$ , while the salt concentration ranged from 0.001 mM to 2 M. In order to form LCGO free stand films via the modified LCGO with chloride salts, it was essential to choose appropriate salt concentration that facilitated this. Through investigation it was established the minimum salt concentration that facilitated free standing film formation was  $\geq 0.08 \text{ mM}$ . The mixtures were stirred by a vortex mixer for 2 min and then directly used to form films using a doctor blade device (K-CONTROL-COATER-System K 303, Model 625). The films were formed onto ITO substrates at a coating speed rate of  $0.5 \text{ m min}^{-1}$  at laboratory temperature, and then samples were dried in oven for 10 h at  $50^\circ \text{C}$ . Unmodified LCGO films were prepared as controls following the same procedure as above. In the control specimens Milli-Q water was used instead of the salt solution to obtain the same LCGO concentration in final dispersions ( $3 \text{ mg ml}^{-1}$ ). To remove the m-LCGO hydrogel films and LCGO films from their substrate, samples were placed in Milli-Q water for 1 h then carefully peeled off from the substrate surface.

### 2.2. Characterization of LCGO and m-LCGO dispersions and films

A TA rheometer (AR-G2) was used to study the rheological properties of LCGO and m-LCGO dispersions. Viscosity of dispersions were measured at  $25^\circ \text{C}$  with a cone-plate geometry (diameter: 40 mm, angle:  $2^\circ$ ), with shear rate ranging from  $10^{-2}$  to  $10^2 \text{ s}^{-1}$ . Time sweep oscillation tests were carried out at  $25^\circ \text{C}$  and constant strain and frequency (0.01, 1 Hz), using the same cone-plate geometry set up. Zeta potential measurements were performed on LCGO and m-LCGO dispersions with a Malvern Zeta sizer Nano series instrument. Raman spectroscopy was carried out on LCGO and m-LCGO films using a Jobin Yvon Horiba HR800 Raman microscope, utilizing a 632 nm laser line and a 300-line grating. X-ray powder diffraction (XRD) analysis of the LCGO and m-LCGO films were conducted using GBC MMA diffraction instrument (GBC Scientific Equipment Pty Ltd, Australia) equipped with  $\text{Cu-K}\alpha$  radiation. The mechanical properties of dry LCGO film and wet m-LCGO hydrogel films were tested using a Shimadzu mechanical tester (EZ-L). The samples for mechanical testing were prepared by laser cutting films (Versa Laser VLS4.60) into strips of 5 mm wide and 15 mm long. The tensile properties of sample strips were measured at a constant strain rate of  $0.01 \text{ mm min}^{-1}$ , and tests were performed on at least 7 replicates of each sample. The tensile strength, elongation at break and Young's modulus were reported as the average of all measurements. Scanning electron microscopy (SEM) images were taken with a field-emission SEM instrument (JEOL JSM-7500FA). Samples were frozen in liquid nitrogen, fractured and sputter-coated (EDWARDS Auto 306) with a thin layer of gold (12 nm thickness). LCGO samples for measuring average sheets size via SEM image were prepared by depositing LCGO sheets on a silanized silicon wafer (300 rim  $\text{SiO}_2$  layer) to ensure good adhesion. Silane solution was prepared by mixing (3-aminopropyl) triethoxysilane (Sigma-Aldrich) with Milli-Q water (1:9 v/v) followed by addition of  $30 \mu\text{l}$  hydrochloric acid (32%, Sigma-Aldrich). After washing with water and ethanol and drying at room temperature, the silicon wafer was silanized by immersing it in the silane solution for 30 min followed by washing with Milli-Q water

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