

Liquid crystals of aqueous, giant graphene oxide flakes†

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We report the observation of liquid crystals formed by giant graphene oxide flakes (aspect ratio above 10 000) suspended in water. As their concentration increases, the flakes undergo transitions from an isotropic dispersion to a biphasic system and then to a discotic nematic liquid crystal. The gel-like liquid crystal displays an unusual defect-free uniform director alignment over hundreds of micrometres. We characterize the nematic order parameter, optical birefringence and elastic properties of this novel mesomorphic system.

Colloidal suspensions of anisotropic particles have been the subject of continued research for over 100 years, owing to their rich variety of liquid crystalline phases and fascinating phase transitions.¹ Initial studies on the orientational ordering, optical, and elastic properties of liquid crystals (LCs) were performed primarily on suspensions of rod-like particles.^{2–5} Onsager⁴ noted that liquid crystallinity is not restricted to only rod-like building blocks, but should also extend to other anisotropic shapes, like disks and platelets. Experimental realization of disk and platelet LC systems, however, was achieved much later⁶ and has been a topic of intense research since that time.^{7,8} In the mid 1960s, mesophases of disk-like molecules were observed during the high temperature carbonization of graphitizable substances such as petroleum and coal tar pitches.⁹ Their complex, polydisperse composition, consisting of multi-component polyaromatic molecules, likely impeded a detailed investigation of this naturally occurring “carbonaceous mesophase”. The first experimental observation of discotic mesophase in a pure, single-component organic molecule system was reported in 1977 by Chandrasekhar *et al.*⁶ They prepared a number of benzene-hexa-*n*-alkanoates, compounds with rigid aromatic cores and flexible

aliphatic side chains, and used optical and X-ray studies to unambiguously demonstrate the existence of discotic LCs.

order of magnitude lower than what has been achieved for discotic mesogens. Optical methods are used to reveal the alignment of GGO flakes in the ordered phase, and measure the birefringence and order parameter; scaling law provides an estimate for the Frank elastic constant of this novel discotic LC system. Controlled confinement and colloidal inclusions are employed to induce LC defects and elastic distortions in the GGO director field.

Much like in the case of polymers and single wall carbon nanotubes (SWNTs), the liquid crystalline phase of graphene and graphene oxide is an important precursor for fabrication of high performance multifunctional aligned fibers. Discotic LCs of graphitic hydrocarbons are also attractive for applications in advanced electronics.²² Both mechanical and electrical properties of such graphene based macrostructures are expected to improve with increasing aspect ratio of individual molecules; similar scaling has already been demonstrated for the structurally similar SWNTs.²³ Therefore, LC suspensions of high aspect ratio graphene are of strong practical interest. From a fundamental point of view, these systems could be the closest experimental realization of theoretical models based on infinitely thin and high aspect ratio rigid platelets.^{24,25}

The GGO flakes were prepared by the method of Ref. 26 These monolayer GGO flakes tend to have a more regular structure and larger continuous regions of intact basal plane, compared to graphene oxide produced using other conventional techniques like Hummer's method.²⁷ The presence of functional groups such as epoxy, hydroxyls, carbonyls, and carboxylates render the flakes hydrophilic. The average size and polydispersity of GGO flakes was characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM), as shown in Fig. 1. The GGO flakes had irregular polygonal shapes with a few ribbon-like structures (additional images in supplementary information†). They had a number-average equivalent diameter $\langle d \rangle$ of 12 μm with relative standard deviation $\sigma_d = (\langle d^2 \rangle - \langle d \rangle^2)^{1/2} / \langle d \rangle$ of 59%. The median aspect ratio of flakes was 10⁴; in comparison, aspect ratio of graphene and graphene oxide in previous reports were: Behabtu *et al.* ~ 700 , Kim *et al.* ~ 1200 and Xu and Gao ~ 2600 .

The phase behavior of aqueous suspensions of GGO flakes was investigated for a concentration range of 0.01–0.14 vol%.

Drops from suspensions with different GGO concentrations were squeezed between a cover slip and a glass slide whose edges were sealed with epoxy glue. These samples were examined using a bright field transmission-mode optical polarizing microscope

a continuous increase of concentration of GGO flakes in the suspension. Upon observation of birefringent textures, the tube ends were sealed with epoxy glue to prevent further drying. Fig. 2 (e) shows an optical micrograph under crossed polarizers of a high concentration GGO suspension prepared using this procedure. Uniform brightness across the entire field of view indicates a well-aligned director (n) over large length scales (hundreds of microns or more). Moreover, it indicates that the GGO flakes are oriented perpendicular to the wide top and bottom sides of the rectangular capillary (since flakes parallel to the top and bottom sides of the capillary would not produce birefringent textures). It is important to note that the observed flake alignment with respect to the top and bottom sides of

distortions using the “red plate” revealed “homeotropic” surface anchoring for *n*, *i.e.* GGO flakes exhibit tangential alignment to the melamine resin particles. The orientation of GGO flakes around melamine resin particles is likely influenced by acid–base interactions between the -NH_2 and =

- 15 F. M. van der Kooij and H. N. W. Lekkerkerker, *J. Phys. Chem. B*, 1998, **102**, 7829–7832.
- 16 D. van der Beek and H. N. W. Lekkerkerker, *Europhys. Lett.*, 2003, **61**, 702–707.
- 17 S. Y. Liu, J. Zhang, N. Wang, W. R. Liu, C. G. Zhang and D. J. Sun, *Chem. Mater.*, 2003, **15**, 3240–3241.
- 18 M. C. D. Mourad, E. J. Devid, M. M. van Schooneveld, C. Vonk and H. N. W. Lekkerkerker, *J. Phys. Chem. B*, 2008, **112**, 10142–10152.
- 19 N. Behabtu, J. R. Lomeda, M. J. Green, A. L. Higginbotham, A. Sinitskii, D. V. Kosynkin, D. Tsentelovich, A. N. G. Parra-Vasquez, J. Schmidt, E. Kesselman, Y. Cohen, Y. Talmon, J. M. Tour and M. Pasquali, *Nat. Nanotechnol.*, 2010, **5**, 406–411.
- 20 J. E. Kim, T. H. Han, S. H. Lee, J. Y. Kim, C. W. Ahn, J. M. Yun and S. O. Kim, *Angew. Chem., Int. Ed.*, 2011, **50**, 3043–3047.
- 21 Z. Xu and C. Gao, *ACS Nano*, 2011, **5**, 2908–2915.
- 22 L. Schmidt-Mende, A. Fechtenkötter, K. Mullen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, **293**, 1119–1122.
- 23 N. Behabtu, M. J. Green and M. Pasquali, *Nano Today*, 2008, **3**, 24–34.
- 24 M. A. Bates and D. Frenkel, *J. Chem. Phys.*, 1999, **110**, 6553–6559.
- 25 R. Eppenga and D. Frenkel, *Mol. Phys.*, 1984, **52**, 1303–1334.
- 26 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. noJ.266Tf78.98810Td{ACS}-292.26(Lett.)TJ/R249[2497Tf62.07390Td{,}-306.206(20099.963.907(24–34.)(4J/R97.9

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SEM images of GGO flakes

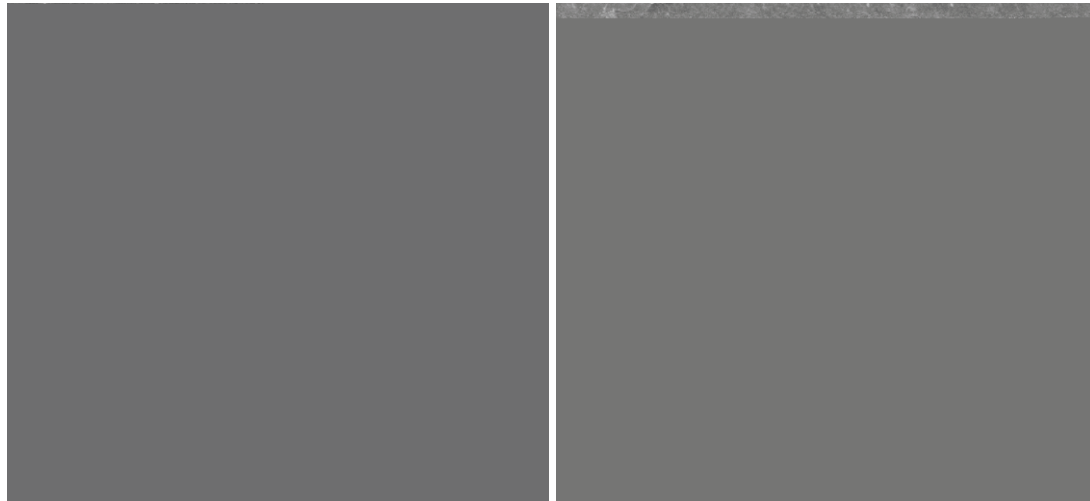


Figure S1: