

## Graphene Oxide Liquid Crystals for Reflective Displays Without Polarizing Optics (Postprint)

**Authors:** He, LQ, Ye, J, Shuai, M, Zhu, Z, Zhou, XF, Wang, YA, Li, Y, Su, ZH, Zhang, HY, Chen, Y, Liu, ZP, Cheng, ZD, Bao, JM

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### Abstract

The recent emergence of liquid crystals of atomically thin two-dimensional (2D) materials not only has allowed us to explore novel phenomena of macroscopically aligned 2D nanomaterials but also has provided a route toward their controlled assembly into th

### Full Text

### Preamble

Figure 1 [Figure 1: see original paper] illustrates two distinct methods for creating and displaying arbitrary features on the surface of graphene oxide (GO) liquid crystals (LCs). The process begins with a clear, dark surface characterized by weak backscattering (Fig. 1a). From this dark background, bright surface regions can be generated (Fig. 1b), enabling the formation of both straight (Fig. 1c) and curved (Fig. 1d) lines in either dark or bright regions. The experimental setup for illuminating and imaging these GO LCs is shown photographically and schematically in Fig. 1e and f. Recent demonstrations of electric-field manipulation of GO flake orientation have further advanced the controlled assembly of 2D nanomaterials for diverse scientific and technological applications.<sup>18</sup> The GO flakes used in this study were synthesized in two separate laboratories using slightly different procedures, both employing chemical exfoliation based on Hummers' method.<sup>19–21</sup> GO liquid crystals were prepared by dispersing these flakes in deionized water. As demonstrated in Fig. 1a–d, arbitrary high-contrast surface textures can be created on GO LC surfaces and conveniently captured using the reflective imaging configuration shown in Fig. 1e and f. These textures can be generated and imaged in two complementary modes: either as reflective bright features on a dark background, or as dark features on a reflective bright surface. Unless otherwise specified, no polarizers were employed in creating these images.

## Surface Texture Creation and Characterization

Figure 2 [Figure 2: see original paper] and its four insets present additional examples of surface textures and symbols. As with most systems requiring external illumination, the visual appearance of these manually created surface textures is strongly dependent on lighting and imaging conditions; these particular photographs were captured under natural sunlight using a commercial Canon EOS60D camera. The size of the GO flakes may also contribute to the observed differences in brightness and contrast between Fig. 1 and Fig. 2. Specifically, the average flake size in Fig. 2 is  $8\ \mu\text{m}$ ,<sup>19</sup> whereas the flakes in all other figures average  $15\ \mu\text{m}$ .<sup>20</sup> These surface textures and letters were drawn manually using a thin stick or wire, analogous to writing with a pen or stylus. Figure 3 [Figure 3: see original paper] illustrates the preparation of a GO LC for writing and the resulting effect on GO flake orientation.

Figure 3a and b depict two types of featureless surfaces with weak light scattering. In Fig. 3a, GO flakes are randomly oriented in three dimensions, yielding an optically isotropic solution. In Fig. 3b, the flakes are vertically oriented with their directors freely rotating in the X-Y plane; the GO LC shown in Fig. 1a exemplifies this configuration. To create a large-area bright reflective surface, one can simply sweep a stick parallel to the LC surface, which reorients the flakes to lie nearly parallel to the surface (with directors aligned along the Z direction). Figure 3c illustrates this surface sweeping effect on initially random flake orientations, and importantly, this bright surface creation mechanism works regardless of the initial flake orientation. Figure 1b provides a clear example of a bright surface generated from a dark one.

To create a dark line on a bright reflective surface, the stick is held vertically in the GO LC and slid in any direction, as depicted in Fig. 3d. This motion aligns flakes vertically along the sliding path, which is precisely how the dark lines and curves in the bright regions of Fig. 1c and d are produced. The bright lines and curves in those same figures are created using the same surface sweeping technique described for Fig. 3c, but with a smaller flat tip.

The vertical flake alignment along a dark line can be conveniently verified using polarizing optics. The line appears bright in transmission when both polarizers are rotated  $45^\circ$  from the line orientation, but becomes dark when one polarizer is parallel to the line, confirming the vertical alignment. This orientation is further substantiated by the anisotropic optical absorption of GO flakes. Figures 4e and f [Figure 4: see original paper] show transmission images with incident light polarized perpendicular and parallel to the flake plane, respectively. The pronounced transmission difference arises primarily from anisotropic absorption: absorption intensifies when the light's electric field lies in the flake plane.<sup>17</sup> The flake alignment is most readily observed in unpolarized transmission imaging; as shown in Fig. 4d, the line appears brighter than its surroundings, revealing that the dark line in reflection is actually more optically transparent. The stronger optical transmission through stick-aligned flakes is not due to reduced

flake concentration. Like reflective displays, GO LCs can function equally well for transmissive displays without polarizing optics.

Figure 4 Images of a straight line in reflection and transmission. (a) Reflection and (d) transmission with unpolarized light. (b, c) Transmission images between two cross polarizers. (e, f) Transmission images with incident light polarized (e) perpendicular to or (f) parallel to the line.

## Rewritable Properties

The creation of a bright surface, as shown in Fig. 3c, can be considered an erasure action. Combined with the writing process illustrated in Fig. 3d, this enables repeated generation and erasure of dark surface textures on a bright background. To demonstrate this rewritable capability, we performed a series of write-erase cycles. As shown in Fig. 5 [Figure 5: see original paper], previous patterns become nearly invisible in reflection after each erasure. However, transmission images between cross-polarizers before and after writing (Fig. 5a and f) reveal that the writing effect persists. This contrast between reflection and transmission occurs because erasure only aligns GO flakes near the surface, while reflective imaging is sensitive solely to surface flakes, whereas writing aligns flakes both near and below the surface. Local erasure of small features can be achieved using a pen with a smaller tip.

Figure 5 Rewritable and erasable characters of GO LC. (a) Transmission image of nearly isotropic LCs between two cross polarizers before line drawing. (b-e) Reflective images of the same GO LC surface after the sequence of write-erase-write-erase. (f) Transmission image of GO LCs in (e).

## Alignment Mechanism

The alignment of GO flakes is induced by shear flow created by relative motion between the stick and the liquid. Such alignment has been previously demonstrated with GO LCs and nanowires.<sup>17,22-24</sup> Although the active moving object in our system is the stick rather than the LC itself, the effect is identical. As reported by Guo et al.,<sup>22</sup> GO flakes form concentric layers driven by homeotropic anchoring on the stick surface and become aligned in the flow wake behind the stick.

This alignment mechanism remains valid for curved stick paths, as shown in Fig. S1.† Flow alignment is also utilized to create vertically oriented GO flakes; as shown in Fig. 3b, flakes align along a glass capillary tube when GO solution is injected into a petri dish. Their orientations persist as the liquid spreads, though the vertical alignment is less perfect than that achieved by stick alignment, evident from the white background in Fig. 1a. The imperfect flow alignment is reflected in a low order parameter of 0.4, compared to 0.8 or higher in typical liquid crystals.<sup>17</sup> In contrast, aligned GO flakes such as those in Fig. 4 exhibit order parameters as high as 0.7.

## Optical Properties and Contrast Mechanisms

As previously discussed, flakes aligned perpendicular to the LC surface appear dark in reflection, while those parallel to the surface exhibit stronger reflection and appear bright. This enhanced reflection originates from multiple GO flakes forming domains; thus, the flake schematics in Fig. 3 do not necessarily represent individual flakes. Such mesoscopic ordering results from mutual flake interactions and represents a fundamental property of liquid crystals. Since GO flakes have lateral dimensions on the order of 10  $\mu\text{m}$ —much larger than visible wavelengths—these flake stacks or domains can be treated as reflective mirrors. Unlike specular reflection from a flat mirror, however, scattering from GO flakes is highly diffuse, making brightness and contrast largely independent of illumination and imaging angles. We attribute this diffuse reflection primarily to two factors: (1) GO flakes are not perfectly flat, possessing wrinkles or folds, and (2) the flakes have varying orientations and are not perfectly parallel to the surface, despite their average directors being aligned along Z.

The dark appearance of vertically oriented GO flakes indicates weak backscattering, arising from a combination of shape anisotropy, dielectric anisotropy, and macroscopic ordering. First, backscattering is weak because the effective scattering cross-section is small when light strikes flake edges—a mechanism analogous to the strong absorption and black appearance of surfaces with vertically grown nanowires.<sup>25</sup> Second, since the out-of-plane dielectric constant and refractive index are smaller than their in-plane counterparts, out-of-plane polarized light experiences reduced backscattering, lowering total backscattered intensity. Finally, strong light scattering originates from density, structural, and index fluctuations. Aligned GO domains become more transparent and scatter less than randomly oriented flakes (Fig. 3a), a property frequently observed in LCs<sup>26,27</sup> and exploited in smart windows that are transparent when LC domains are electrically aligned but diffuse and milky when randomly oriented.<sup>28</sup>

High optical anisotropy is a unique property of atomically thin 2D materials, where the in-plane dielectric constant typically exceeds the out-of-plane value—a characteristic not shared by many other nanomaterials like nanowires.<sup>25</sup> Graphene exemplifies this behavior;<sup>16</sup> its out-of-plane refractive index approaches unity, while the in-plane index has a larger real component and substantial imaginary part, enabling polarization-sensitive absorption for broadband polarizers. Graphene oxide flakes inherit this optical anisotropy, though the precise refractive index of individual GO flakes remains unreported<sup>17,29</sup> and may depend on synthesis method and other factors. The bright and dark appearance of line patterns in Fig. 4e and f provides direct evidence of GO flake anisotropic absorption.

The strong unpolarized transmission in Fig. 4d arises primarily from reduced optical absorption (Fig. 4e), though reduced scattering through the more ordered GO region also contributes.

## Concentration and Polarization Effects

To summarize, contrast between bright and dark features in GO LC reflective displays results from multiple contributions—scattering, absorption, and transmission—as exemplified in Fig. 6a [Figure 6: see original paper] and b. While vertically aligned GO flakes appear dark in any reflective display, closer examination reveals that lines are darker and thicker when polarization is parallel to the line. Based on in-plane versus out-of-plane optical constant differences, backscattered light should be stronger when incident light is parallel to the line or flake planes, theoretically producing brighter lines in Fig. 6a than in Fig. 6b. We attribute this discrepancy to multiple scattering from flakes beneath the LC surface. Light perpendicular to the line penetrates deeper, with some backscattering from subsurface flakes or the petri dish bottom contributing to total backscattered intensity and lightening the line appearance.

This combined effect explains contrast evolution with GO weight concentration. Figure 6c-h show images of similar lines in GO solutions ranging from low to high concentration. Contrast becomes pronounced only at concentrations of 0.05 wt% and diminishes below 0.05 wt% or above 0.4 wt%. Low-concentration suspensions exhibit weak contrast because both reflection and absorption are weak due to fewer aligned flakes. At 0.05 wt%, lines fail to appear dark because of low absorption and significant subsurface backscattering, as discussed above. At very high concentrations, solution viscosity increases dramatically, hindering flake reorientation and alignment.

Previous studies have shown that GO solutions below 0.05 wt% are isotropic, while higher concentrations exhibit increasing nematic phase fraction.<sup>17,18,22</sup> Such concentration-dependent phase transitions are readily observed by monitoring aligned flake dynamics (Fig. S2-4†). The initially bright line fades in approximately 90 s for 0.01 wt% solutions but persists longer at higher concentrations, showing no obvious decay at 0.05 wt%. This concentration-dependent retention time enables selection of optimal flake concentrations for specific applications.

These observations demonstrate that ordered structures can be temporarily created in otherwise isotropic solutions, and conversely, isotropic phases can be generated in nematic LCs. Such isotropic phases are frequently produced when preparing 0.2 wt% GO LCs by manually shaking the solution in the petri dish. Except for surface flakes partially aligned parallel to the surface, interior flakes adopt random orientations (Fig. 3a). This isotropic phase exhibits strong light scattering but no birefringence, as shown in Fig. 4 and 5. When the dish is shaken to spin the liquid slowly in one direction, vortex patterns like those in Fig. 2 emerge, provided the concentration exceeds 0.4 wt%. Note that liquid near the petri dish wall shows weak backscattering because it remains stationary relative to the bulk solution.

## Device Implications

We have demonstrated repeated manual writing of dark features on bright backgrounds (Fig. 5), and similar creation of bright features on dark backgrounds (Fig. 1) is also achievable, though erasing or preparing a dark surface requires GO solution extraction and injection through a capillary tube. Recent demonstrations of electric-field GO flake alignment have resolved this erasure limitation.<sup>18,30</sup> Using techniques similar to those in Boogie Board and other LC displays, GO flakes can be vertically aligned between transparent electrodes by applied voltage, enabling devices analogous to Boogie Boards or electronic blackboards. It should be noted that while electric fields cannot permanently fix GO flake directors, they can align them in the pattern shown in Fig. 3b when applied between the LC's top and bottom surfaces.

## Conclusions

In conclusion, we have created GO flakes with different macroscopic orientational ordering using mechanical flow alignment and systematically studied their optical responses—including backscattering, absorption, and transmission—under various light polarizations. We have established and explained the relationship between scattering and GO flake orientation, and demonstrated a reflective display using GO LC as a rewritable medium. Since shape and optical anisotropy are fundamental properties of 2D materials, the observed phenomena and demonstrated applications are transferable to any 2D nanomaterial. The ability to create macroscopically ordered structures from individual flakes opens new opportunities for both basic research and device applications of 2D nanomaterials.

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