

Electrically Tunable Scattering from Devitrite–Liquid Crystal Hybrid Devices

Haider Butt,* Ali K. Yetisen, Ammar A. Khan, Kevin M. Knowles, Malik M. Qasim, Seok Hyun Yun, and Timothy D. Wilkinson

Devitrite is normally an unwanted crystalline impurity in the soda-lime-silica glass making process. Thin needles formed by heterogeneous nucleation of devitrite on the glass surface provide unique birefringence properties for potential applications in tunable optical devices. Here, devitrite and a liquid crystal are combined to create an electrically variable optical diffuser. The magnitude and scattering angle of the transmitted light propagating through the diffuser are tuned by varying the voltage between the graphene and indium tin oxide electrodes on either side of the liquid crystal. The threshold voltage to switch the transmitted light from a predominantly horizontal diffusion to a random order is 3.5 V. Angle-resolved measurements show broad diffusion angles of transmitted light with a maximum deflection of $\pm 60^\circ$. The dynamically tunable devitrite-liquid crystal hybrid devices may advance the development of currently less viable technologies including beam shaping and automatic light transmission control.

storage, screens and monitors, imaging systems, medical devices, and optical sensors. The capability to incorporate active elements to control the transmitted light profile and intensity is highly desirable in photonic devices. Engineering an electrically tunable optical diffuser which combines devitrite (Dev), historically a waste material in glass manufacturing, a liquid crystal (LC), a material more commonly used in televisions and smartphones, will be a unique advance in creating active optical elements.^[2] Devitrite, the morphology of which consists of fans of needle-like crystals that can extend up to several millimeters in length, is able to diffuse light at wide angles, enabling it to be an efficient diffuser.^[3] LCs, on the other hand, consist of self-assembled birefringent material which can be used for

phase modulation when a voltage is supplied.^[4] Here, a voltage-controlled tunable optical device has been engineered by combining Dev and LCs. The present work reports the capability of this device to diffuse light and the control of its magnitude based on the amount of supplied voltage.

Devitrite, $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$, is a distinctive crystalline phase that is produced when soda-lime-silica glass undergoes prolonged heat treatment at 900°C .^[5] It has long been considered an undesirable side product in the process of transparent glass making. The methods of discarding devitrite were identified in the 1930s after its identification in the 1920s;^[6] however, the optical properties of devitrite itself were never comprehensively studied. In the morphology used in this work, the devitrite needles are on the order of a few hundred nanometers wide, of the same scale as the wavelength of light. These devitrite needles trigger phase modulation of light because of the difference in refractive index between the needles and the surrounding undevitrified soda-lime-silica glass matrix, as has also been shown recently from a consideration of the phase modulation arising in thin sections of crystalline glazes between willemite needles and the surrounding siliceous glass matrix.^[6] As a consequence of the scale of the microstructure and the arrangement of the needles in three dimensions, light can be diffused to high scattering angles.^[3] Microscope images of fans of needle-like crystals nucleated at the glass surface and then grown into the bulk glass, where the fans overlap in three dimensions are shown in **Figure 1a,b**. In comparison with existing optical diffusers, devitrite is a low-cost material. It also has the potential to be utilized

1. Introduction

Optical diffusers spread light evenly across a surface, minimizing or removing high-intensity bright spots.^[1] They have applications in aerospace, the military, encrypted information

Dr. H. Butt
School of Engineering
University of Birmingham
Birmingham B15 2TT, UK
E-mail: h.butt@bham.ac.uk

Dr. A. K. Yetisen, Prof. S. H. Yun
Harvard Medical School and Wellman Center
for Photomedicine
Massachusetts General Hospital
65 Landsdowne Street, Cambridge, MA 02139, USA

Dr. A. K. Yetisen, Prof. S. H. Yun
Harvard-MIT Division of Health Sciences and Technology
Massachusetts Institute of Technology
Cambridge, MA 02139, USA

A. A. Khan, Dr. M. M. Qasim, Prof. T. D. Wilkinson
Centre of Molecular Materials for Photonics and Electronics
Department of Engineering
University of Cambridge
9 J.J. Thomson Avenue, Cambridge CB3 0FA, UK

Dr. K. M. Knowles
Department of Materials Science and Metallurgy
University of Cambridge
27 Charles Babbage Road, Cambridge CB3 0FS, UK



DOI: 10.1002/adom.201600414

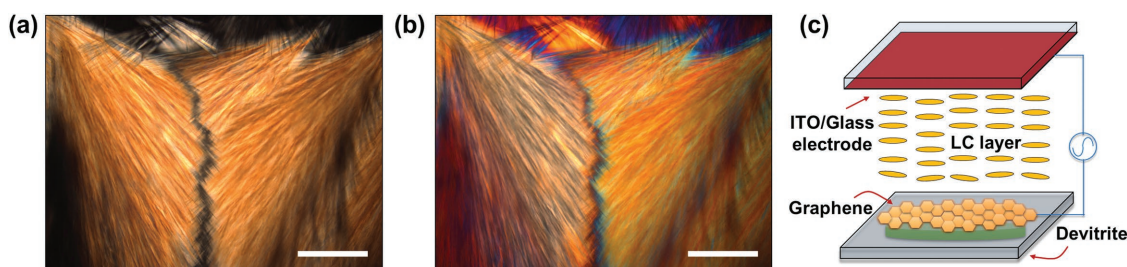


Figure 1. Devitrite-based tunable optical diffusers. a) Polarized light microscope image showing different arrangements of devitrite crystals within a 30 μm thin slice of heat-treated soda-lime-silica float glass. Scale bar = 500 μm . b) The image of the region in (a) taken with a sensitive tint wave plate inserted at 45° to the polarizer and probe. Scale bar = 500 μm . c) Schematic of the tunable devitrite-LC electro-optical device.

in commercial applications such as optical imaging, photovoltaics, photolithography, displays, light-emitting diodes (LEDs), and photodynamic therapy.^[2,7]

On its own, devitrite has limited suitability for being implemented as an optical device because there is no control over the direction of its fans of crystals which scatter light randomly. However, with the implementation of liquid-crystal displays (LCDs), the scattering of light can be tuned when a voltage is supplied. Conventionally, an electro-optical device containing nematic LCs can be manufactured with two parallel transparent electrode structures, having a sandwiched LC layer. We have previously used thin films of polymer wrapped single-walled carbon nanotubes as transparent electrodes to incorporate LCs in order to achieve optical scattering.^[8] However, in the present work, we have used a slice of devitrified glass as the diffusing medium, coating its surface with a single layer of graphene (Gr) to achieve electrical conductivity (Figure 1c). In comparison with carbon nanotube electrodes, graphene layers have superior electrical and optical properties.^[9]

2. Results and Discussion

2.1. Fabrication of the Tunable Devitrite-LC Optical Diffuser

Preparation of the tunable diffuser involved using graphene as a 2D conducting material. This structure has atomic thickness and demonstrates high crystallographic quality and ballistic electron transport.^[10] Graphene is a suitable material for optoelectronic devices due to its high chemical stability, optical transmittance, flexibility, and mechanical strength. A graphene electrode was fabricated by creating graphene through a low-pressure chemical vapor deposition (LPCVD) process on commercial cold-rolled Cu foils (25 μm thick).^[11] The Cu foil was etched by FeCl_3 (0.5 M) and the monolayer graphene was transferred to glass substrates using a sacrificial polystyrene layer.^[9]

To produce an optoelectronic device, a LC cell was assembled using two substrates (Figure 1c). These substrates acted as electrodes for a nematic LC layer (BL006), which was chosen to maximize the scattering potential of the device because of its strong polarity with a birefringence of $\Delta n = 0.29$ at 24 °C. The top electrode consisted of an indium tin oxide (ITO) coated glass substrate. The lower electrode was the graphene sheet

deposited on a slice of devitrified glass. Ni contacts were placed at the end of the graphene layer to connect it to an external voltage source. The two substrates/electrodes were assembled together with a UV-curable adhesive in the presence of spacer beads to achieve a uniform cell thickness of 8.7 μm .

2.2. Optical Characterization of the Tunable Devitrite-LC Diffuser

To analyze the optical diffusion properties, a semi-transparent hemispherical screen 15 mm in diameter was positioned above the fabricated tunable diffuser (Figure 2a). A red laser beam (633 nm, 4.5 mW, 1 mm in diameter) was used to illuminate the sample normally from the bottom. The resultant far-field diffusion patterns were collected over the hemispherical screen as the voltage (peak to peak (pp)) was increased from 0 to 8.0 V. When the beam was transmitted through the tunable diffuser, the light was scattered at large angles and strong optical diffusion changes were observed as the voltage was gradually increased. The voltage was applied to the sample using a signal generator that controlled the frequency of the signal. This experiment enabled real-time measurements of the transmitted diffused light and aided in determining the range of threshold voltage for the tunable diffuser. Variation in voltage also allowed for tuning of the far-field diffusion patterns on the hemispherical screen. The most significant changes in the transmitted light patterns were at 2–3 V, where the LC molecules start to re-orient in response to the applied electric field. Schematics of the working principle of the device, where LC molecules are mostly in a planar alignment at low voltages, are shown in Figure 2c. The diffusion patterns are mostly dictated by the arrangement of needle-shaped devitrite crystals. The sample area had two overlapping ponytail-like fans of devitrite crystals, which produced a predominant diagonal diffusion of light. The changes in the diffusion patterns were measured by angle-dependent intensity readouts and also captured using a digital camera. At the light intensity change was most pronounced along the horizontal direction.

2.3. Measurements of Tuned Light Intensity

A photodetector was used to detect the normal intensity of light (i.e., at 0° from the normal) when a laser beam passed

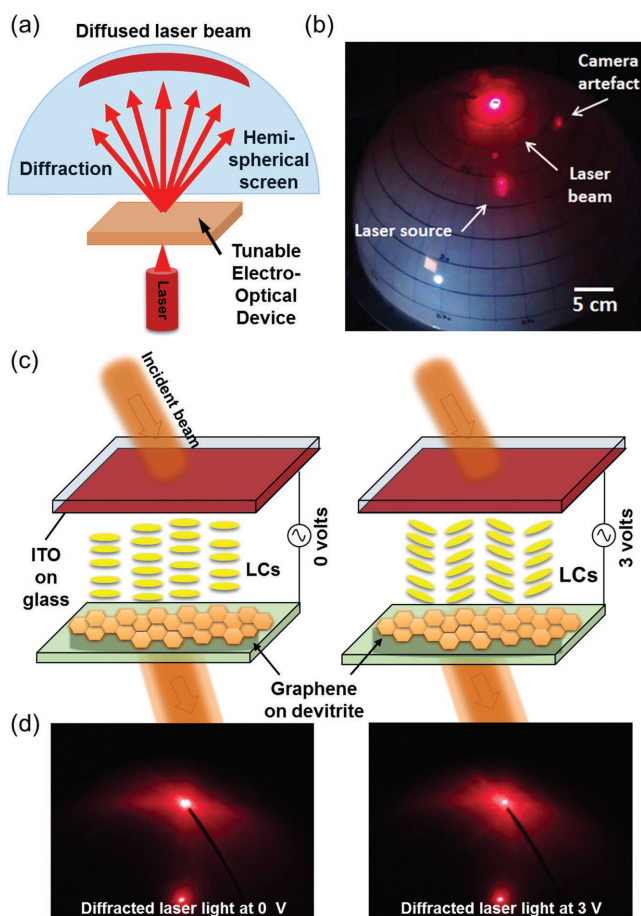


Figure 2. Optical characterization of the tunable devitrite-LC diffuser. a) Schematic of the experimental setup used to capture the transmitted light patterns from the tunable diffuser. b) Laser beam passing through regular glass and illuminating an area on the hemispherical screen. c) Schematic of tunable optical device when laser light passes through the device at different applied voltages. d) Diffusion patterns collected over the screen as the voltage in the graphene layer was increased from 0 to 3 V.

through the devitrite-LC diffuser at different voltages (0–8 V). The polarization of the laser beam transmitting through the sample was altered to determine the effect of polarization on the threshold voltage and diffusion efficiency. Initially, the experiments were performed with a Gr-LC cell without devitrite (Figure S1, Supporting Information). The normalized transmission intensities subtly changed as the voltage and polarization were altered. The voltage-dependent normalized transmission intensity results for the hybrid Gr-Dev-LC device are shown in Figure 3. The effect of polarization and propagation direction into the device was analyzed. For light passing through Dev-Gr-LC-ITO respectively, a significantly low light intensity at 3.5 V (threshold voltage) was measured for both polarizations. The normalized intensities were near 0.00174 and 0.001734 for the horizontal and vertical polarizations, respectively (Figure 3a,b). This signified that near 3.5 V, LCs have switched from a predominantly planar alignment (at 0 V) to a more disordered texture when an electric field was

applied that increased the refractive index disorder inside the LC cell. An increase in light scattering resulted in low transmission intensity at 0° from the normal. As the voltage was increased, the LC molecules aligned vertically, decreasing the scattering effect, so that an increase in zero order transmission was measured. The LC domains were aligned with the random structures of the polycrystalline graphene (Figure 3e,f). Polarization sensitivity might be attributed to the devitrite layer due to the different orientations of the crystal needles, which renders the light scattering polarization dependent. Additionally, graphene is known to produce some alignment effects in the LC layers.^[9] Graphene electrodes may dictate the molecular alignments within the LC subdomains, contributing to the polarization sensitivity.

2.4. Angular Diffusion Measurements

The angular diffusion of light was quantified as the voltage was varied in increments (Experimental Section “Angle-Resolved Measurements of Light Intensity”). The angular intensity profiles measured for a horizontally polarized laser passing through the device in order Dev-Gr-LC-ITO are shown in Figure 4. The angular plots show a dominant peak at 0° from the normal representing the zero order beam. However, the angle-resolved measurements for 3.0 V showed that the maximum light diffusion occurred as the transmitted light was spread to $\pm 60^\circ$ with full width at half maximum (FWHM) of $\approx 25^\circ$. The results agree with the previous experiments (at 0° only), where the normalized intensity reached a minimum at 3.0 V (Figure 4a,b), while the normalized intensity might be larger in this case due to the distance of the laser being closer to the photodetector. At higher voltages, the device did not diffuse light and a dominant zero order peak was measured. Control experiments were conducted with a LC device without devitrite where no light diffusion was measured. The angular measurements shown in Figure 4c show a predominant zero order of undiffused laser light. No significant voltage-dependent diffusion was observed.

Polycrystalline, polymer-supported graphene has a multi-domain alignment layer for nematic LCs.^[9] The LCs align (in-plane) with the randomly oriented graphene domains, leading to refractive index mismatch at domain boundaries, and causing optical scattering. An applied voltage of 3 V to an $8.7 \mu\text{m}$ cell filled with BL006 is insufficient to cause complete switching from a planar alignment to a homeotropic alignment; however, the field is large enough to cause deformations in the LC texture. It is hypothesized that the initial splay deformations (at low applied electric fields) of the micrometer-sized LC domains leads to an increase in refractive index disorder, leading to an increase in scattering. At higher applied electric field magnitudes, the amount of scattering induced by the graphene alignment/electrode reduces as more domains align with the applied electric field, reducing the disorder and optical scattering. The devitrite layer has been shown to diffuse laser light to large angles. The optical characteristics of devitrite combined with the tunable scattering nature of the Gr-ITO device allow the formation of a hybrid light scattering device.

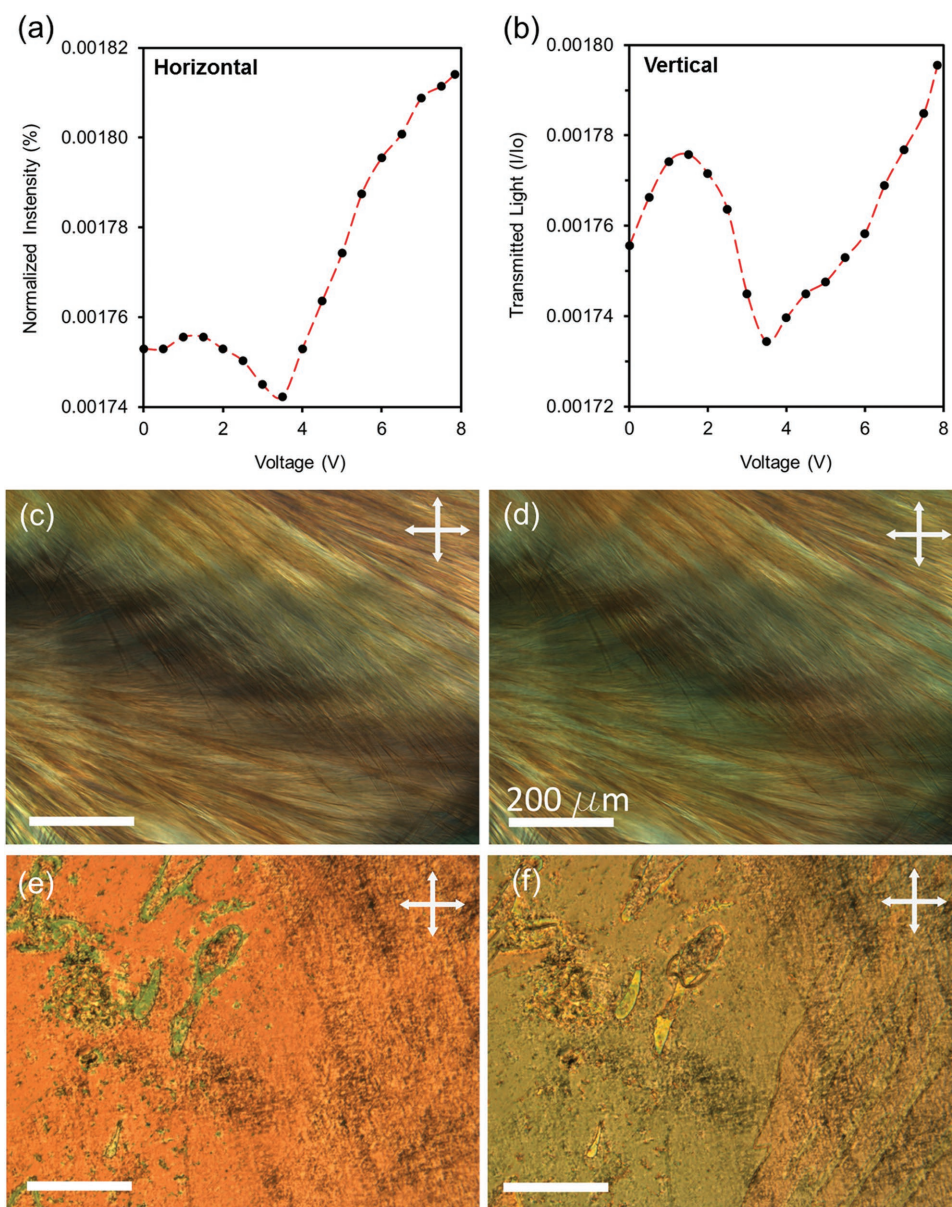


Figure 3. Measurements of normal light transmission through the hybrid Dev-Gr-LC device at 0° from the normal. Normalized intensity against peak to peak voltage changes when a) a horizontally and b) a vertically polarized laser passes through the device in order Dev-Gr-LC-ITO. Cross-polarized microscopy images showing c,e) unswitched and d,f) switched states of the device in Dev-Gr-LC-ITO and Gr-LC-ITO regions.

3. Conclusion

Devitrite as a low cost material has been used in an LC device to efficiently diffuse light by tuning the supplied voltage. The optimum operation properties including tunable light intensity and diffusion ranges were determined as a function of voltage. The threshold voltage was determined to be 3.5 V, which produced the lowest zero order intensity and the highest angular scattering. A large diffusion angle of light was achieved using horizontally polarized light. The polarization of the laser affected the direction of laser light diffusion. The technology described here can also be employed in LEDs to diffuse saturated light.

Devitrite has a cross-sectional diffusion area when crystals intersect, which could be implemented in the device for diffusion in both horizontal and vertical directions for application in tunable lighting of large areas (e.g., stadiums, smart windows). These devices can also be integrated with angle-intolerant diffraction gratings,^[12] biosensors,^[13] holographic displays,^[14] data encoders, and security devices^[15] to broaden the viewing angles. In addition, horizontal diffusion could be applied to headlights in vehicles to produce larger diffusion angles in horizontal direction while reducing the intensity of the headlamp. The devitrite diffusers can be fabricated in different geometries and integrated with LCs to act as tunable beam shapers or holographic diffusers.

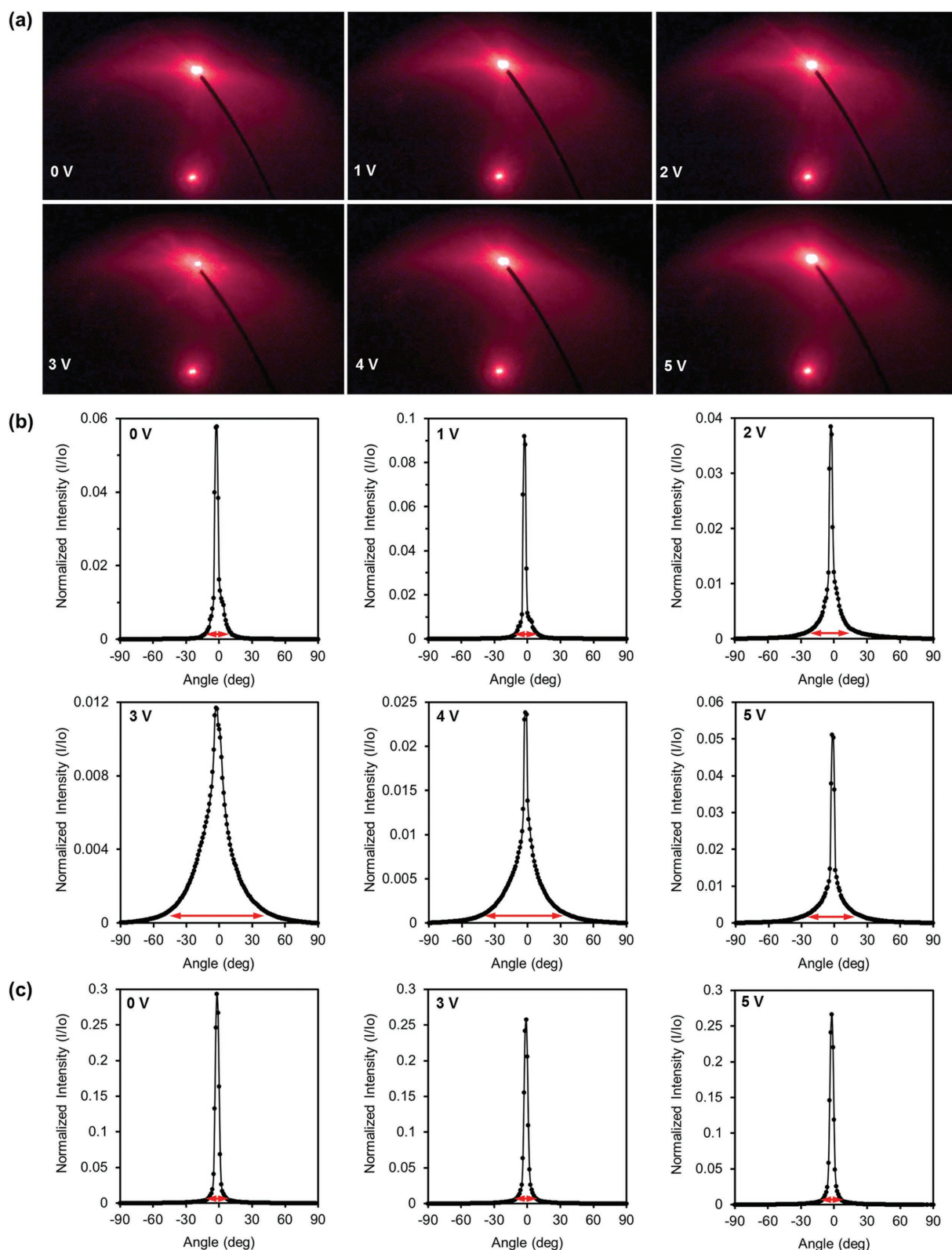


Figure 4. Transmitted light intensities at different applied peak to peak voltages. a) Horizontal beam diffusion intensities as a function of angle for the device in horizontal polarization through the Dev-Gr-LC-ITO. b) The angular diffusion measurements through the Dev-Gr-LC-ITO. c) Normalized horizontal intensity distribution as a function of angle where laser light passes through Gr-LC-ITO (control), showing light diffusion at different peak to peak voltages.

4. Experimental Section

Fabrication of the Tunable Diffuser: Fabrication of the graphene electrode involved the synthesis of a monolayer graphene through a LPCVD on commercial cold-rolled Cu foils (Alfa Aesar Puratronic, 99.9% purity, 25 μm thick). Following the synthesis, the monolayer graphene was relocated to glass substrates using a polystyrene support layer and an aqueous solution of FeCl_3 (0.5 M) to etch the Cu foil followed by several rinses in DI water. The polystyrene layer with graphene was then transferred to the glass substrate and dried. The polystyrene support was dissolved with ethyl acetate, and the samples were washed in isopropanol and blow dried in nitrogen.

To fabricate the tunable diffuser, a LC cell was assembled between two electrode substrates. A nematic LC layer (BL006, birefringence $\Delta n = 0.29$ at 24 $^\circ\text{C}$) was sandwiched between the electrodes. The top substrate had an ITO and glass electrode. The second (lower) electrode had a graphene conductor located on a devitrified glass electrode. The two substrates were glued together with an optically curable adhesive (Norland NOA68) mixed together with spacer beads (Merck), which provided a uniform cell thickness of 8.7 μm . No alignment layers were used. LC and graphene were used as they are organic and therefore the reactions in their bonds can be thoroughly studied when incorporated into the tunable optical device. Electrical wire connections were assembled between the two substrates using an indium solder. Finally, devitrite was attached on the top layer by spin casting it on the graphene-glass.

Characterization of the Optical Properties: To detect the intensity of the scattered light when a red laser light passes through the optical device at different voltages, the change of light intensity was measured. This experimental setup had a laser which was placed directly below the sample at predetermined positions while a photodetector was placed directly above the sample (15 cm away) and connected to an optical power meter. A signal generator was used to change the voltages (Figure S2, Supporting Information). The increments of the pp voltage were performed from 0.0 to 8.0 V at a step size of 0.5 V. The sample was then placed in a stationary position normal to the laser beam. The voltage was increased and the reading on the power meter was recorded. The position of the laser light on the sample was altered while the experiment was repeated to determine the effect of polarization when laser light propagated through the sample. This experiment determined the ability of the device to control the intensity of light by scattering and diffuse the laser light, therefore reducing and increasing the intensity of light through the LCD. Through this experiment, the exact threshold voltage was determined while the influence of polarization was studied at the same time by changing the direction of the laser light perpendicularly propagating over the device.

Angle-Resolved Measurements of Light Intensity: The angular distribution of laser light after it passes through the tunable optical device was determined. A goniometer setup was used to measure the optical intensity as laser light scattered after passing through the device. The goniometer setup consisted of a red laser pointer, a glass slide to fix the tunable optical diffuser, a photodetector, and an optical power meter to detect and display the intensity of the laser light at different angles. The setup was controlled by a motor to run the setup which was controlled by computer software. The device was placed in the center of the goniometer setup and the red laser was illuminated at normal incident angle. An optical power meter fixed on a rotating arm on the other side of the sample was used to perform the angular measurements. The rotating arm had the flexibility to rotate by 180 $^\circ$ around the sample. Each experiment was repeated seven times to get data from 0.0 to 6.0 V. The experiment was also repeated on the device with the laser light shining on the device at different polarizations.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

H.B. and A.K.Y. thank the Leverhulme Trust for research funding. The authors also thank the Royal Society and EPSRC IAA Follow on Fund for supporting this research. The authors thank Dr. Aydin Sabouri, Chern Wong, and Prof. Stephan Hoffman for discussions and research assistance.

Received: May 29, 2016

Revised: August 30, 2016

Published online: October 18, 2016

- [1] M. Christophersen, B. F. Philips, *Appl. Phys. Lett.* **2008**, 92, 194102.
- [2] G. M. Morris, T. R. M. Sales, U.S. Patent 7,033,736, **2006**.
- [3] H. Butt, K. M. Knowles, Y. Montelongo, G. A. J. Amaratunga, T. D. Wilkinson, *ACS Nano* **2014**, 8, 2929.
- [4] a) R. Rajasekharan-Unnithan, H. Butt, T. D. Wilkinson, *Opt. Lett.* **2009**, 34, 1237; b) T. D. Wilkinson, H. Butt, Y. Montelongo, *Nanoscience with Liquid Crystals*, Springer, Switzerland **2014**, p. 1.
- [5] K. M. Knowles, R. P. Thompson, *J. Am. Ceram. Soc.* **2014**, 97, 1425.
- [6] a) A. B. Peck, *J. Am. Ceram. Soc.* **1926**, 9, 351; b) K. M. Knowles, H. Butt, A. Batal, A. Sabouri, C. J. Anthony, *Opt. Mater.* **2016**, 52, 163.
- [7] J. M. Kim, P. S. Dutta, *Sol. Energy Mater. Sol. Cells* **2012**, 103, 35.
- [8] A. A. Khan, G. D. M. R. Dabera, H. Butt, M. M. Qasim, G. A. J. Amaratunga, S. R. P. Silva, T. D. Wilkinson, *Nanoscale* **2015**, 7, 330.
- [9] M. M. Qasim, A. A. Khan, A. Kostanyan, P. R. Kidambi, A. Cabrero-Vilata, P. Braeuninger-Weimer, D. J. Gardiner, S. Hofmann, T. D. Wilkinson, *Nanoscale* **2015**, 7, 14114.
- [10] X.-T. Kong, A. A. Khan, P. R. Kidambi, S. Deng, A. K. Yetisen, B. Dlubak, P. Hiralal, Y. Montelongo, J. Bowen, S. Xavier, K. Jiang, G. A. J. Amaratunga, S. Hofmann, T. D. Wilkinson, Q. Dai, H. Butt, *ACS Photonics* **2015**, 2, 200.
- [11] a) X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, *Science* **2009**, 324, 1312; b) X. Li, C. W. Magnuson, A. Venugopal, R. M. Tromp, J. B. Hannon, E. M. Vogel, L. Colombo, R. S. Ruoff, *J. Am. Chem. Soc.* **2011**, 133, 2816.
- [12] H. Butt, A. K. Yetisen, D. Mistry, S. A. Khan, M. U. Hassan, S. H. Yun, *Adv. Opt. Mater.* **2016**, 4, 497.
- [13] a) N. M. Farandos, A. K. Yetisen, M. J. Monteiro, C. R. Lowe, S. H. Yun, *Adv. Healthcare Mater.* **2015**, 4, 792; b) C. P. Tsangarides, A. K. Yetisen, F. da Cruz Vasconcellos, Y. Montelongo, M. M. Qasim, T. D. Wilkinson, C. R. Lowe, H. Butt, *RSC Adv.* **2014**, 4, 10454; c) A. K. Yetisen, H. Butt, S.-H. Yun, *ACS Sens.* **2016**, 1, 493; d) A. K. Yetisen, Y. Montelongo, M. M. Qasim, H. Butt, T. D. Wilkinson, M. J. Monteiro, S. H. Yun, *Anal. Chem.* **2015**, 87, 5101; e) A. K. Yetisen, Y. Montelongo, F. da Cruz Vasconcellos, J. Martinez-Hurtado, S. Neupane, H. Butt, M. M. Qasim, J. Blyth, K. Burling, J. B. Carmody, *Nano Lett.* **2014**, 14, 3587; f) A. K. Yetisen, H. Butt, F. da Cruz Vasconcellos, Y. Montelongo, C. A. Davidson, J. Blyth, L. Chan, J. B. Carmody, S. Vignolini, U. Steiner, *Adv. Opt. Mater.* **2014**, 2, 250; g) A. K. Yetisen, Y. Montelongo, N. M. Farandos, I. Naydenova, C. R. Lowe, S. H. Yun, *Appl. Phys. Lett.* **2014**, 105, 261106; h) A. Yetisen, M. Qasim, S. Nosheen, T. Wilkinson, C. Lowe, *J. Mater. Chem. C* **2014**, 2, 3569; i) M. Humar, S. J. Kwok, M. Choi, A. K. Yetisen, S. Cho, S.-H. Yun, *Nanophotonics* **2016**, 5, 60; j) A. K. Yetisen, H. Butt, L. R. Volpatti, I. Pavlichenko, M. Humar, S. J. Kwok, H. Koo, K. S. Kim, I. Naydenova, A. Khademhosseini, S. K. Hahn, S. H. Yun, *Biotechnol. Adv.* **2016**, 34, 250;

- k) A. K. Yetisen, I. Naydenova, F. da Cruz Vasconcellos, J. Blyth, C. R. Lowe, *Chem. Rev.* **2014**, *114*, 10654; l) M. Zawadzka, T. Mikulchik, D. Cody, S. Martin, A. K. Yetisen, J. L. Martinez-Hurtado, H. Butt, E. Mihaylova, H. Awala, S. Mintova, *Photonic Materials for Sensing, Biosensing and Display Devices*, Springer, Switzerland **2016**, p. 315.
- [14] a) Y. Montelongo, A. K. Yetisen, H. Butt, S. H. Yun, *Nat. Commun.* **2016**, *7*, 12002; b) A. K. Yetisen, Y. Montelongo, H. Butt, *Appl. Phys. Lett.* **2016**, *109*, 061106.
- [15] a) Q. Zhao, A. K. Yetisen, C. J. Anthony, W. R. Fowler, S. H. Yun, H. Butt, *Appl. Phys. Lett.* **2015**, *107*, 041115; b) F. d. C. Vasconcellos, A. K. Yetisen, Y. Montelongo, H. Butt, A. Grigore, C. A. Davidson, J. Blyth, M. J. Monteiro, T. D. Wilkinson, C. R. Lowe, *ACS Photonics* **2014**, *1*, 489; c) A. K. Yetisen, H. Butt, T. Mikulchik, R. Ahmed, Y. Montelongo, M. Humar, N. Jiang, S. Martin, I. Naydenova, S. H. Yun, *Adv. Opt. Mater.* DOI: 10.1002/adom.201600162 **2016**; d) Q. Zhao, A. K. Yetisen, A. Sabouri, S. H. Yun, H. Butt, *ACS Nano* **2015**, *9*, 9062.
-