Graphene-Based Liquid Crystal Device

Peter Blake,[†] Paul D. Brimicombe,[‡] Rahul R. Nair,[‡] Tim J. Booth,[§] Da Jiang,[||]
Fred Schedin,[||] Leonid A. Ponomarenko,[‡] Sergey V. Morozov,[⊥] Helen F. Gleeson,[‡]
Ernie W. Hill,[†] Andre K. Geim,[||] and Kostya S. Novoselov*,[‡]

*School of Computer Science, University of Manchester,
Manchester M13 9PL, United Kingdom, School of Physics & Astronomy, University of
Manchester, Manchester M13 9PL, United Kingdom, Graphene Industries Limited,
32 Holden Avenue, Whalley Range, Manchester M16 8TA, United Kingdom,
Centre for Mesoscience and Nanotechnology, University of Manchester,
Manchester M13 9PL, United Kingdom, and Institute for Microelectronics Technology,
142432 Chernogolovka, Russia*

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ABSTRACT

Graphene is only one atom thick, optically transparent, chemically inert, and an excellent conductor. These properties seem to make this material an excellent candidate for applications in various photonic devices that require conducting but transparent thin films. In this letter, we demonstrate liquid crystal devices with electrodes made of graphene that show excellent performance with a high contrast ratio. We also discuss the advantages of graphene compared to conventionally used metal oxides in terms of low resistivity, high transparency and chemical stability.

Graphene is the first example of truly two-dimensional materials.[1] Only one atom thick, it demonstrates high crystallographic quality[2] and ballistic electron transport on the micrometer scale.[1] Such unique properties make it a realistic candidate for a number of electronic applications. In particular, graphene is an attractive material for optoelectronic devices, in which its high optical transmittance, low resistivity, high chemical stability, and mechanical strength seems to make it an ideal optically transparent conductor.

Transparent conductors are an essential part of many optical devices. Traditionally, thin metallic or metal oxide films are used for these purposes (for a review see ref 3). At the same time, there is a constant search for new types of conductive thin films, as existing technologies are often complicated (e.g., thin metallic films require antireflection coating[3]) and expensive (often using noble or rare metals). Furthermore, many of the widely used metal oxides exhibit nonuniform absorption across the visible spectrum[4] and are chemically unstable (for instance, the commonly used indium tin oxide (ITO, In_2O_3:Sn) is known to inject oxygen[5] and indium[6] ions into the active media of a device). Recently carbon nanotube films have been produced[7] and used as an alternative transparent conductor in various photonic devices including electric-field-activated optical modulators,[7] organic solar cells,[8] and liquid crystal displays.[9] The experimental discovery of graphene[10] brought a new alternative to the ubiquitous ITO. The optical properties of this material are now being widely tested,[11–15] and graphene films have recently been used as transparent electrodes for solar cells.[16]

In this letter, we report on the use of graphene as a transparent conductive coating for photonic devices and show that its high transparency and low resistivity make this two-dimensional crystal ideally suitable for electrodes in liquid crystal devices. We will also argue that graphene, being mechanically strong, chemically stable, and inert, should improve the durability and simplify the technology of potential optoelectronic devices.

Graphene flakes were prepared by micromechanical cleavage[10,17] on a glass microscope slide. They were first located using an optical microscope[18] (Figure 1f,g) and then further identified as monolayer graphene using Raman microscopy.[19] Thin (55 nm) chromium/gold contacts were then deposited around the flakes, so the graphene crystal was effectively covering a window in the metallization, Figure 1a,b (this geometry also eliminates stray electric fields from the edges of the electrode). Planar-aligned liquid crystal devices were then fabricated using such graphene-on-glass films as one of the transparent electrodes, Figure 1a. The other substrate was of a glass slide coated with conventional ITO. Both substrates were coated with a polyvinyl alcohol alignment

* Corresponding author. E-mail: kostya@manchester.ac.uk. Telephone: +44-(0)161-275-41-19. Fax:+44-(0)161-275-40-56.
† School of Computer Science, University of Manchester.
‡ School of Physics & Astronomy, University of Manchester.
§ Graphene Industries Limited.
|| Centre for Mesoscience and Nanotechnology, University of Manchester.
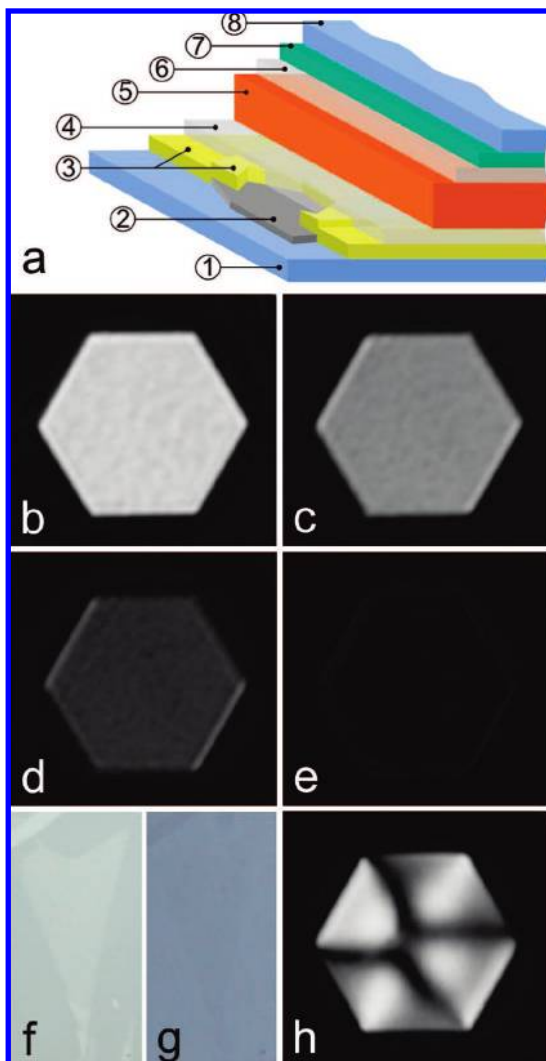⊥ Institute for Microelectronics Technology.

Figure 1. (a) Schematic diagram of our liquid crystal devices with typical layer thicknesses in brackets: 1, glass (1 mm); 2, graphene; 3, Cr/Au contact surrounding graphene flake (5 nm Cr + 50 nm Au); 4, alignment layer (polyvinyl alcohol) (40 nm); 5, liquid crystal (20 μm); 6, alignment layer (40 nm); 7, ITO (150 nm); 8, glass (1 mm). The graphene flake is surrounded by a nontransparent Cr/Au contact. (b−e) Optical micrographs of one of our liquid crystal devices using green light (505 nm, fwhm 23 nm) with different voltages applied across the cell: (b) $V = 8$ Vrms; (c) $V = 13$ Vrms; (d) $V = 22$ Vrms; (e) $V = 100$ Vrms. Overall image width is 30 μm. The central hexagonal window is covered by graphene, surrounded by the opaque Cr/Au electrode. (f) An optical micrograph (in reflection, using white light) of a graphene flake on the surface of a 1 mm thickness glass slide. The contrast is of the order of 6%. Overall image width is 10 μm. (g) The same image but in transmission. The flake is practically invisible. (h) Control device with no graphene in the opening of the Cr/Au contacts with $V = 100$ Vrms applied across the cell. Because the electrode on the ITO-coated surface is continuous, there is a significant stray field within the window that distorts the liquid crystal structure, leading to the pattern shown.

layer that was subsequently baked and then unidirectionally rubbed (ITO-coated substrate only) in order to promote uniform alignment of the liquid crystal director. The device was then capillary-filled with nematic liquid crystal material E7 (Merck). Applying a voltage across the liquid crystal layer distorts the crystal alignment, changing the effective bire-
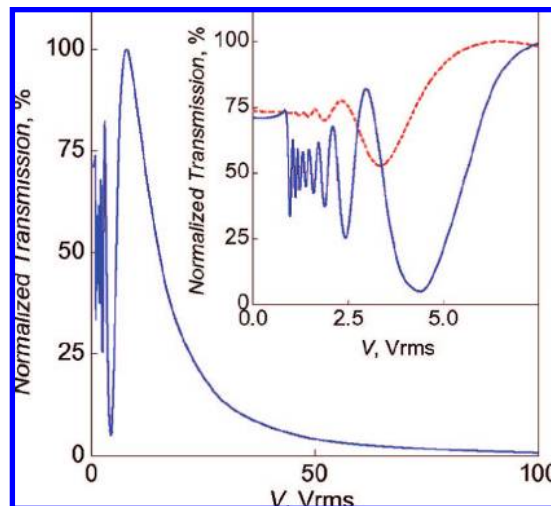

Figure 2. Light transmission through the liquid crystal device as a function of voltage applied across the cell, normalized to the maximum transmission. Inset: the same at low voltages. Solid blue curve: in green light, 505 nm, fwhm 23 nm; dashed red curve: in white light. The data taken in white light practically coincide with those in green light for voltages above 10 Vrms and are omitted from the main panel for clarity. From the oscillatory behavior the thickness of the liquid crystal layer is estimated to be $\sim$20 μm, assuming that the birefringence of E7 is 0.225.

fringence of the device and altering the transmitted light intensity.[20] A control sample, with an opening in the metallization not covered by graphene, was also prepared (Figure 1h). Note that, although we will limit our consideration of graphene-based liquid crystal devices to those with planar untwisted nematic liquid crystals, this technology could equally be applied to any of the various nematic liquid crystal device types (e.g., twisted nematic,[21] supertwisted nematic,[22] in-plane switching,[23] and vertically aligned nematic[24] devices) and also to ferroelectric and other liquid crystal devices that use smectic phases.

An ac (square-wave) voltage was applied across the cells in order to reorient the liquid crystal director. The electrooptic properties were observed using an optical microscope with the device placed between crossed polarizers and the rubbing direction oriented 45° with respect to the polarizers. Above the expected threshold voltage of around 0.9 Vrms, a strong change in the transmission is observed (Figures 1b−e, 2) both in white and monochromatic light. The fact that the whole electrode area changes contrast uniformly suggests that the electric field is applied uniformly through the area of graphene and that the graphene has no negative effect on the liquid crystal alignment. The contrast ratio (between maximum transmission and the transmission when 100 Vrms is applied across the cell) is better than 100 under illumination using white light, which is very good for this type of cell and demonstrates that graphene could indeed be used effectively as a transparent electrode for liquid crystal displays. No significant changes in transmission were observed for the control sample, with only edge effects appearing due to the finite thickness of the cell, Figure 1h.

We will now assess the quality of our liquid crystal devices, concentrating on such important issues as the
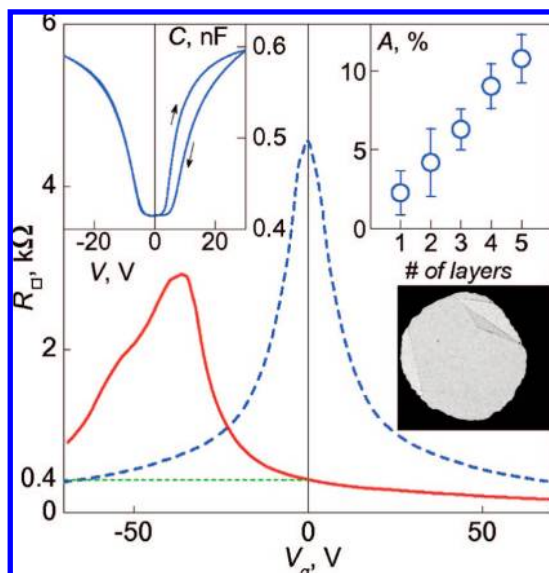
Figure 3. Sheet resistance of a graphene device as a function of gate voltage with (solid red curve) and without (dashed blue curve) a layer of polyvinyl alcohol on top. Polyvinyl alcohol provides n-type doping, shifting the curve to negative gate voltages. The sheet resistance at zero gate voltage is ~400 Ω. Left inset: capacitance of one of our liquid crystal devices as a function of voltage applied. Right inset: light absorption of suspended graphene of different thicknesses. The bottom picture represents a TEM micrograph of a 30 μm aperture covered by suspended graphene used in these experiments. Light absorption by graphene could be measured as a contrast between the area covered by the material and the empty space: there is a gap on the left and folded area (top right). Similar suspended structures of few-layer graphene has been prepared and studied in the experiment.

transparency of graphene, its resistivity, and chemical stability. Light absorption by this two-dimensional material has been studied on suspended mono- and few-layer graphene flakes. In such samples, graphene covers an aperture (about 30 μm in diameter) in metallic foil so that light transmission could be measured directly (further details can be found in ref 15). The results are presented in Figure 3 (right inset) as a function of the number of layers. Each layer of graphene absorbs about 2%, which is significantly lower than that of conventionally used ITO (15−18%[3]).

The sheet resistance of undoped graphene is of the order of 6 kΩ (one conductivity quantum per species of charge carriers[1]). However, it can be reduced down to 50 Ω by chemical doping,[10,25] and even unintentional doping (due to molecules absorbed from the surrounding atmosphere, e.g., water)[10] can be of the order of 10^{12} cm^{-2}. In liquid crystal devices, an electrode is usually in direct contact with an alignment layer (in our case polyvinyl alcohol). We have tested the doping of graphene with polyvinyl alcohol by preparing a standard graphene device on a 300 nm SiO$_2$/Si wafer and measuring its gate response with and without a layer of polyvinyl alcohol on top of graphene (Figure 3). The introduction of a layer of polyvinyl alcohol produces n-type doping of about 3×10^{12} cm^{-2}. For this particular sample, it resulted in a drop in the sheet resistance down to 400 Ω, which is an impressive result for a conductive coating with optical transmission of about 98%. It is difficult to

compare this result to ITO, as the resistance of In$_2$O$_3$:Sn films diverges strongly (on the order of tens of kΩ) when trying to obtain optical transmittance above 95%. ITO films with 95% transmittance demonstrate comparable sheet resistances of a few hundred Ohms, dropping to tens of Ohms at an optical transmittance of about 90%.[26] Similar or even lower resistances can be achieved for graphene by a variety of means: increasing the number of layers,[27] intentional doping, or by using samples with higher mobility.[28,29] It is evident from Figure 3 (right inset) that even five layers of graphene absorb only ≈10% of light, which is well inside the industrially relevant limit.

An important issue for most ITO-based liquid crystal devices and other photonic devices is the chemical stability of the metal oxide and the diffusion of ions into the active media. Such processes deteriorate the active media (for example via oxidation if oxygen is injected[5]) and can lead to breakdown at lower voltages. Furthermore, in liquid crystal displays, the injected ions get trapped at the alignment layer, thus screening the applied electric field. This leads to the so-called image sticking problem,[30] which is usually avoided by driving the liquid crystal cells with alternating voltage.

One can generally expect that such issues can be avoided when using graphene, where its chemical stability should minimize the level of ion diffusion. To check this, we have measured the capacitance of one of our liquid crystal devices, which has one electrode made of graphene and the other from ITO, when applying dc voltages of different polarities (Figure 3 left inset, here positive voltage corresponds to higher potential on the ITO electrode). There is clearly a highly hysteretic response when applying positive biases, but no hysteresis has been observed at the opposite polarity. We attribute this observation to positive indium ions drifting into the liquid crystal from the ITO electrode, whereas no ions are injected from the graphene electrode. Similar liquid crystal devices constructed using ITO electrodes on both substrates produce the hysteretic response for both polarities.

Although it is important to demonstrate the possibility and advantages of using graphene as a transparent conductive coating, the feasibility of its mass production is essential when considering realistic applications. No industrial technology can rely on the micromechanical cleavage technique that allows only minute quantities of graphene and, although sufficient for fundamental research and proof-of-concept devices, is unlikely to become commercially viable. Recently, large-area conductive films have been demonstrated by using chemical exfoliation of graphite oxide and then reducing it to graphene.[16,31,32] This could lead to a viable way of making thin graphene-based films with properties similar to those discussed earlier and using them for various photonic devices. However, so far this technique has not demonstrated the ability to fully recover the excellent conductive properties of graphene.[33] We propose an alternative approach. It involves making a graphene suspension by direct chemical exfoliation of graphite (rather than graphite oxide), which is subsequently used to obtain transparent conductive films on top of glass by spin- or spray-coating.

Crystals of natural graphite (Branwell Graphite Ltd.) were exfoliated by sonication in dimethylformamide (DMF) for over 3 h. DMF "dissolves" graphite surprisingly well, and the procedure resulted in a suspension of thin graphitic platelets with large proportion of monolayer graphene flakes, DMF also wets the flakes preventing them from conglomerating.[34] The suspension was then centrifuged at 13000 rpm for 10 min to remove thick flakes. The remaining suspension consists mostly of graphene and few-layer graphite flakes of submicrometer size. The thickness of the exfoliated flakes has been verified by atomic force microscopy and transmission electron microscopy (Figure 4a). Both techniques indicate high proportion of monolayer flakes (up to 50%).

The suspension was spray-deposited onto a preheated glass slide (Figure 4b,c) that yielded thin (~1.5 nm) films over centimeter sized areas, which consisted of overlapping individual graphene and few-layer graphene flakes. These films were then annealed for 2 h in argon(90%)/hydrogen(10%) atmosphere at 250 °C. The transparency of these graphitic layers was approximately 90% (Figure 4c), which is expected for 4−5 layers of graphene coverage (Figure 3, right inset) and is still well within the margins of being relevant for industrial applications.

To measure the resistivity of our films, a mesa structure in the shape of the Hall bar with typical dimensions of 1 mm was prepared, and the four-probe resistance was measured as a function of temperature (Figure 4d). The high temperature region (above 10 K) is well described by $\exp(T_0/T^{1/3})$ dependence, characteristic for variable range hopping in two dimensions.[35] The room temperature sheet resistance is of the order of 5 kΩ, which, together with the high transparency of 90%, is already acceptable for some applications[3,16] and can be decreased further by increasing the film thickness. Resistance at low temperatures deviates from the variable-range-hopping dependence but can be described by the simple activation dependence $\exp(-\Delta/T)$ (see inset in Figure 4d). We attribute this low-temperature behavior to weak tunneling-like coupling between overlapping flakes, possibly due to contamination with organic (DMF) residues. The procedure we used can also modify the chemical termination of the dangling bonds of our graphene crystallites, which might affect the transport properties of the films obtained (although on a lesser level than the contamination between the overlapping flakes). This indicates some potential for improvements as better cleaning and annealing procedures may improve the coupling between graphene crystallites and decrease the film resistance further.

To conclude, high optical transparency, low resistivity, and high chemical stability of graphene makes it an excellent choice for transparent electrodes in various optoelectronic devices. Furthermore, there are already several technologies that potentially allow mass production of thin graphene-based transparent conductors (besides the chemical exfoliation of graphite described in the present letter, one can also think of epitaxial growth of graphene on top of a metal surface, followed by a transfer of such a layer onto a transparent substrate[1]). These techniques are capable of producing continuous graphene films of thickness
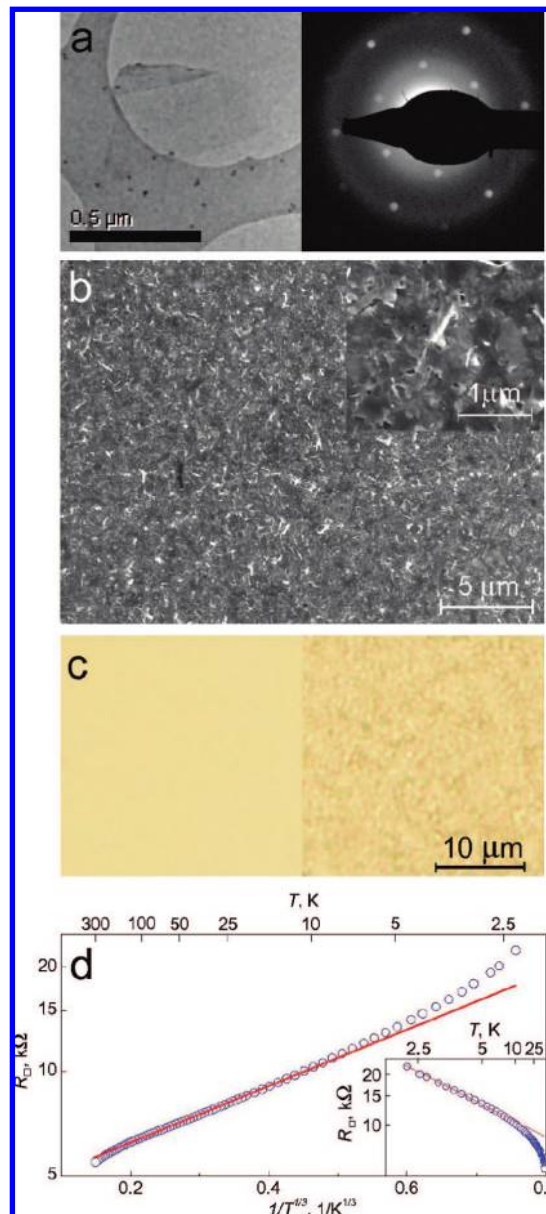

Figure 4. (a) TEM image (left panel) and electron diffraction pattern (right pannel) of a graphene flake obtained by the chemical exfoliation method. Equal intensity of first- and second-order diffraction peaks confirms that the flake is exactly one monolayer thick. (b) Scanning electron micrograph of a thin graphitic film obtained by chemical exfoliation and spray-coating. Inset shows the same area under higher magnification. (c) Light transmission through an original glass slide (left) and the one covered with the graphitic film (right). (d) Temperature dependence of the film's sheet resistance ($R \sim \exp(T_0/T^{1/3})$ behavior is observed at $T > 10$ K, where T_0 is a constant[35]). Inset: the same data but for the low temperature interval ($R \sim \exp(\Delta/T)$ behavior is observed at $T < 10$ K, where Δ is a constant). The red lines are guides for the eye.

below five monolayers, which is required for realistic applications.

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