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Graphene electrodes for adaptive liquid crystal contact lenses

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Abstract: The superlatives of graphene cover a whole range of properties: electrical, chemical, mechanical, thermal and others. These special properties earn graphene a place in current or future applications. Here we demonstrate one such application – adaptive contact lenses based on liquid crystals, where simultaneously the high electrical conductivity, transparency, flexibility and elasticity of graphene are being utilised. In our devices graphene is used as a transparent conductive coating on curved PMMA substrates. The adaptive lenses provide a +0.7 D change in optical power with an applied voltage of 7.1 V_{rms} - perfect to correct presbyopia, the age-related condition that limits the near focus ability of the eye.

OCIS codes: (000.0000) General; (000.2700) General science.

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1. Introduction

The potential of graphene as transparent electrodes in liquid crystal (LC) devices was first demonstrated in 2008 by Blake *et al*. [1]. The device exhibited uniform switching and high optical transparency, stringent requirements for display applications, demonstrated for a single pixel of dimensions ~10μm in a conventional geometry with parallel glass substrates. The real advantages of graphene electrodes are apparent in non-conventional geometries, for applications where flexibility and transparency are key requirements and with much larger electrode areas. Graphene, being only one atom thick [2], and having a number of unique electrical [3], mechanical [4] and thermal [5] properties is fully compatible with flexible, curved LC devices. Furthermore, large roll to roll production of graphene [6] makes graphene a realistic candidate to be used in mass-produced flexible optoelectronic devices [7, 8], organic and solid state solar cells [9, 10], supercapacitors [11], neural imaging and opto-genetic applications [12, 13]. Recent advances in fabricating simple and low-cost graphene coated nanoprobes demonstrate the extensive potential graphene exhibits to be used in various applications and progressing its move from lab to market [14].

This paper reports the first application of graphene electrodes in contact lenses with an electrically controllable focus. This adaptive lens exhibits the fastest response time yet reported (sub-second, faster than a blink) with a continuously variable focus. Importantly, we demonstrate that the transparent, conductive and flexible nature of graphene can simplify the contact lens construction, making it an obvious choice of electrodes for such applications.

Electrically switchable LC contact lenses were demonstrated recently [15-18] and represent an exciting addition to the 'smart contact lenses' being proposed by several research groups [19-21]. The underlying concept here is to provide an electrically controllable focus which can correct presbyopia, a condition that affects all adults over the age of fifty and is one of the major concerns in modern optometry. Adaptive contact lenses provide significant advantages in comparison with other treatments such as reading or multifocal spectacles [22]. In the adaptive contact lenses, an electrical signal provides a continuous change in the effective refractive index of the lens, changing the lens power and allowing the user to focus on nearby objects, thereby replicating the accommodation mechanism of the younger eye [15-18]. Unfortunately, the transparent conductive coatings traditionally used in LC devices are rarely compatible with the highly curved and flexible substrates required for adaptive contact lenses, as they quickly lose electrical conductivity.

2. Design and construction of the lens using graphene electrode

The switchable contact lens is made from mating two polymethylmethacrylate (PMMA) substrates with a lens-shaped gap containing a LC, as shown in Fig. 1. The overall optical properties of the LC contact lens and its variable optical power are determined by the geometric lens design, together with the choice of LC and switching mode [15-18].

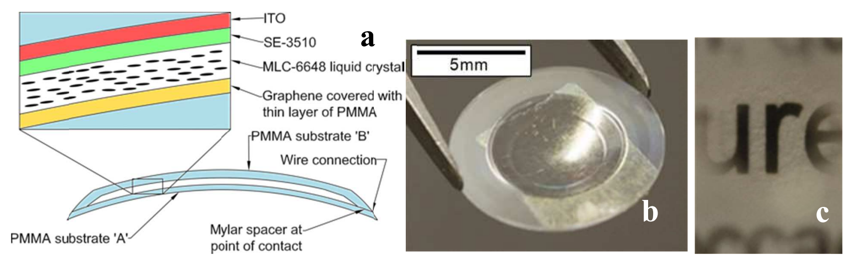

Fig. 1. (a) A schematic diagram of the LC contact lens constructed with a graphene electrode on the convex side of the PMMA substrate 'A' and Indium Tin Oxide (ITO) on the concave side of substrate 'B'. The insert shows construction details (not to scale) with the LC director parallel to the lens substrates (no voltage applied). The convex and concave substrates provide positive optical powers of +6.4±0.1 D and +7.6±0.1 D respectively; the radius of curvature of the lens is 7.8mm, matching the curvature of the human cornea. The thickness of the LC layer between the substrates at the centre of the lens is 50 µm. (b) is a photograph of a contact lens substrate with graphene deposited onto the central curved section of the lens (6 x 6 mm^2) so that whole curved area is active. (c) Demonstrates the excellent transparency from the clarity of the text through the graphene-coated substrate lens. The text seen in focus through the lens demonstrates the optical power of the lens substrate. The average optical transmittance of graphene deposited onto a flat substrate using the same process as used for depositing it on the curved substrates was found to be 98% [1].

The graphene layer used in the construction of the LC contact lens was synthesized using a chemical vapour deposition (CVD) growth technique. The details of the graphene preparation and transfer process are described elsewhere [6]. To transfer the graphene film onto the contact lens, the graphene film formed on one side of copper (Cu) foil was covered with PMMA and the graphene on the other side was removed using oxygen plasma. The PMMA/graphene membrane was then released by dissolving the Cu. After repeated cleaning of the remaining PMMA/graphene layers, the whole PMMA/graphene membrane was transferred onto the PMMA lens substrates. This process results in a high quality graphene film covered with a thin layer (~100 nm) of PMMA, with sheet resistance <1 kΩ/□ that can be used for excellent interconnects in wearable and flexible electronic applications such as contact lenses (Fig. 1b). Contact lenses are usually fabricated as single units, whether by lathing or, more commonly, injection moulding. Sputtering of ITO at the point of lens manufacture is not only expensive, but the curved plastic surfaces lead to issues associated with poor adhesion of ITO onto the substrates, uniformity and yield. In addition, ITO thin films are brittle [23], and therefore unsuitable for flexible applications. The production of graphene on the PMMA substrate and subsequent transfer onto the flexible, curved lens components, offers a clear route to mass production of the adaptive contact lenses.

Here, we used a commercially available nematic LC material (MLC-6648, Merck) exhibiting a positive dielectric anisotropy with a birefringence $\Delta n=0.07$ and relatively a low viscosity, offering the potential for sub-second response time, ideal for a switchable focus contact lens. The LC ordinary refractive index, n_o, is similar to that of the PMMA substrates (1.49 at 633 nm), minimising Fresnel losses.

A key requirement of a LC device is uniform, controlled orientation of the director. In most devices an alignment layer is deposited on both electrodes and rubbed to provide a unique orientation direction. We found that no alignment layer is needed on the graphene substrate as both PMMA and graphene give good planar alignment. The overall preferred orientation in the contact lens is defined by the rubbing direction on the concave substrate, an approach similar to that used in the graphene-based pixel demonstrated by Blake *et al*. [1]. The use of the rubbed polyimide alignment layer necessitated the ITO electrode. We note that for this planar lens geometry, the 'off' state focus is polarization dependent. This feature, as well as methods of overcoming such a dependence are discussed in detail in [15-18].

3. Investigation of lens quality and operation

Several measurements were made to investigate the quality and operation of the lens. Dielectric spectroscopy was used to determine the threshold voltage, V_{th} for switching the lens. On application of a voltage just above V_{th}, the LC director begins to orient parallel to the electric field and the measured device capacitance increases, reaching a maximum at voltage far above the threshold. The V_{th} of the contact lens device was found to be $+2.1\pm0.2$ V_{rms} from voltage-dependent capacitance measurements. This agrees well with the value calculated using the expression for a parallel device: $V_{th}=\pi(k_{11}/\varepsilon_o\Delta\varepsilon)^{1/2}$, where ε_o is the permittivity of free space and k_{11} and $\Delta\varepsilon$ are the splay elastic constant and dielectric anisotropy of the liquid crystalline material respectively. The values for k_{11} and $\Delta\varepsilon$ were measured to be 11.0 ± 1.0 pN and 2.9 ± 0.2 respectively in a separate experiment using a planar aligned LC contained between two parallel glass plates, leading to a calculated value of $V_{th}= 2.1\pm0.2$ V_{rms}.

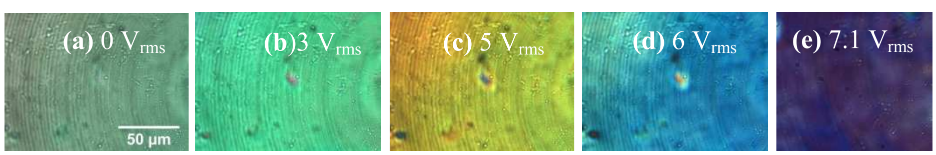

Fig. 2. Textural micrograph images (maximum transmission, i.e. rubbing direction at 45˚ to the crossed polarizers) of the LC contact lens at room temperature as the applied voltage is varied. The change in the birefringence colours can clearly be observed as the voltage increases from (a) 0 V_{rms} to higher voltages (b-e). The images have been taken near the centre of the lens; the faint concentric lines are sub-micron inhomogeneities in the PMMA surfaces caused by circular lathing during manufacture. The scale for all images is as marked on the lower right hand side of Fig. (a).

Polarizing microscopy was used to observe the texture and hence evaluate the quality of the LC alignment in the lenses. The uniform birefringence colours seen in Fig. 2 indicate both excellent planar alignment of the director and uniformity of construction. Fig. 2a shows the textural micrograph while no voltage was applied to the contact lens. Figs. 2b-e clearly show the change in birefringence colours when voltages higher than the threshold (2.1 V_{rms}) were applied. The changing colours with the increasing voltage are associated with the change in the effective birefringence which is in turn due to an effective change in the extraordinary refractive index (n_e) with increasing voltage. These indices were determined in a conventional device from fitting the reflection spectra using the Berreman methodology [24] with further details in Ref. [25]. On application of a high voltage, n_e changes from 1.54 to a minimum of 1.48, which approaches n_o, measured separately as 1.47. Therefore, the application of 7.1 V_{rms} results in a birefringence change of 0.06, successfully demonstrating the change in optical power required for an adaptive contact lens. The micrograph images demonstrate that using a single alignment layer produces a lens with excellent optical quality.

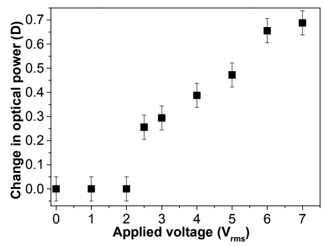

Fig. 3. The voltage-dependence of the change in optical power of the adaptive contact lens. A continuous change in optical power is observed and V_{th} is consistent with capacitance measurements and the optical micrographs.

The focal power of the lens was measured as a function of applied voltage as described previously [15]. Briefly, an expanded 10mW 632.8 nm laser beam was passed through the contact lens and the point of focus was found using a beam profiler. The optical power of the contact lens increases with applied voltage (7.1 V_{rms}) changing by +0.7±0.1 D (Fig. 3). The V_{th} of the contact lens deduced from the optical power measurements was found to be 2.0±0.5 V_{rms}, which again agrees with the capacitive response (V_{th}=2.1±0.2 V_{rms}) and the optical micrographs (Fig. 2). The correction to presbyopes requires an additional optical power and the continuous change in optical power offered by this system offers the possibility of a mid-region correction which is important as it would allow vision correction for applications such as viewing computer screens. The measured change in optical power is in good agreement with that calculated using the thick lens equation. Moreover, an applied voltage of 7.1 V_{rms} results in the maximum optical power change (+0.7±0.1 D).

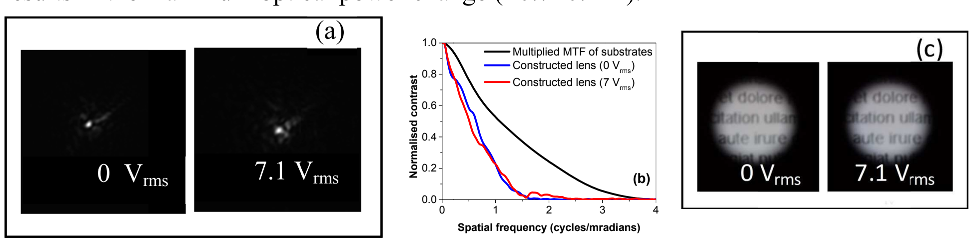

Fig. 4(a) The PSF measurements of the LC contact lens at 0 and 7.1 V_{rms} respectively at the appropriate focal planes. (b) The MTF curves of the LC contact lens compared with that of the substrates. The OFF and ON states of the device exhibit MTF50 values of 0.52 and 0.63 line pairs/mrad respectively. (c) Images of text brought into focus with the LC lens with and without the application of 7.1 Vrms. The relatively small change observed in the two images due to the small optical change of +0.70.1 D.

The optical quality of the contact lens was measured quantitatively using the point spread function (PSF) and the modulation transfer function (MTF). The PSF was captured using a beam profiler placed at the point of focus of the expanded laser beam. Additional lenses were used to correct aberrations induced through the clamping of the contact lens when mounting on the optical rail. The MTF of the lens quantifies its ability to resolve details of different spatial frequencies and was generated by taking the Fourier transform of the PSF. MTF50 values (spatial frequency at 50% modulation) are used for a quantitative comparison of the MTF curves. Fig. 4a shows the PSFs of the contact lens at applied voltages of 0 and 7.1 V_{rms} respectively. Fig. 4b compares MTF curves of the contact lens at different voltages with the combined resolving power of the substrates 'A' and 'B'. MTF50 values for 0 and 7.1 V_{rms} applied are 0.52 and 0.63 lp/mrad respectively demonstrating similar optical quality in both states. The calculated MTF50 for the combined substrate system is 1.1 lp/mrad. We can conclude that though the system is limited by the substrates, the OFF and ON state of the LC lens are comparable making it an excellent first demonstration of a graphene electrode based lens that can correct presbyopia. The optical quality of the contact lens at 0 and 7.1 V_{rms} is qualitatively demonstrated in Fig. 4c by using a DSLR camera. A change in magnification of the text demonstrates the +0.7±0.1 D increase in optical power of the contact lens.

An important parameter for the LC contact lens is the electro-optic response time. This was measured by placing the contact lens on a polarizing microscope and monitoring the change in intensity of monochromatic (632nm) light with a photodiode as the lens was switched 'on'. At 5 V_{rms} the response time, τ_{ON}, was 0.6±0.2 seconds. The response time of a parallel device is given by $\tau_{ON} = \eta d^2/(\varepsilon_0 \Delta\varepsilon V^2 - k_{11}\pi^2)$, where η is the LC viscosity and d the device thickness. τ_{ON} was measured to be 3.5±0.4ms for a 5µm thick parallel device, so a 60µm thick device should have τ_{ON}=0.5±0.1 seconds, is in good agreement with the contact lens response using an average LC layer thickness of 60µm. This measured τ_{ON} is comparable to the blink of an eye (a few hundred milliseconds) which is sufficiently fast for this application; indeed, Pixel Optics marketed LC spectacles with the phrase 'focus as fast as you can blink your eye' [26]. The 'off' time for a parallel device is $\tau_{OFF} = \eta d^2/k_{11}\pi^2$ and we note that our design can improve both the on and off times by reducing the LC layer thickness; a factor of 10 decrease in response time is achieved by reducing the average lens thickness by a factor of ~3.

4. Conclusions

An adaptive LC contact lens with a graphene electrode has been successfully developed with an active area that covers the whole of the curved lens. The optical transparency, flexibility, low resistivity, good adhesion and stability of graphene make it an ideal candidate for use in contact lenses to correct presbyopia. The graphene adhered well to the PMMA substrate and the transmittance through the graphene electrode on the contact lens substrate is comparable to that of ITO. Importantly the flexibility of graphene makes the manufacture of these single contact lens units much easier. Using graphene for the electrodes avoids problems associated with using ITO, namely the requirement of a hard coat layer, expensive sputtering of ITO and low yields.

The lens developed is capable of providing a continuous change in optical power change of up to 0.7±0.1 D, switching the optical compensation continuously between far and near vision. The lens exhibited excellent alignment and optical quality with the use of a single alignment layer. The response time of the device was much less than a second and simple measures such as reducing the LC layer thickness or increasing the driving voltage will achieve response times better than 1/20th second, a typical response time for the human eye.

The potential for graphene electrodes in contact lenses is not just a consequence of the excellent optical and electro-optical performance; using graphene electrodes opens up new possibilities for the manufacture of flexible contact lenses. The flexibility of graphene would be advantageous if applied to soft lenses (hydrogels) which are commonly used contact lens materials. Moreover, the layer of PMMA on the top of graphene would help to inhibit entry of moisture, ions or gases in the lens containing LC. Patterning with graphene is already possible [27] and if applied to the lenses, will make the contact lens assembly much simpler. Our current aim is working towards a self-contained wirelessly operated device which will revolutionise the contact lens industry.

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