Smart Reinvention of the Contact Lens with Graphene

Kyoungjun Choi and Hyung Gyu Park*

Nanoscience for Energy Technology and Sustainability, Department of Mechanical and Process Engineering, Eidgenössische Technische Hochschule (ETH) Zürich, Tannenstrasse 3, Zürich CH-8092, Switzerland

ABSTRACT: With potential benefits to the 71 million contact lens users worldwide, contact lenses are being reinvented in the form of smart wearable electronics. In this issue of ACS Nano, Lee et al. report on the fascinating functions of a graphene-based smart contact lens that is able to protect eyes from electromagnetic waves and dehydration. Graphene and two-dimensional materials can be exploited in many opportunities in the development of smart contact lenses. Here, we briefly review and describe prospects for the future of smart contact lenses that incorporate graphene in their platforms.

In 2014, we saw the “smart” reinvention of contact lenses as an ideal ocular platform for wearable electronics.1 This smart contact lens (Figure 1) aimed to monitor glucose levels in tears to diagnose diseases such as diabetes easily and noninvasively.

Remarkable progress in micro-nanomanufacturing now enables us to imagine that contact lenses could be incorporated with wireless devices and miniaturized sensors. A wireless antenna in the lens could transmit data that are collected and analyzed by sensors and microprocessors, respectively, to external devices such as smart phones, tablet computers, or other wearable devices. A plan also exists to integrate into smart contact lenses a tiny light-emitting device and a built-in camera capable of signaling, recording, and projecting images directly into our field of vision. Although these goals may sound like science fiction, several market leaders today are steadily embodying these concepts.

Early work on contact lenses dates back to 1508: Leonardo da Vinci is credited with conceptualizing a contact lens through a water-filled glass hemisphere over the eye. However, it was not until 1949 that the first corneal lens via poly(methyl methacrylate) (PMMA) was introduced. Despite its glass-like clarity, the bare oxygen permeance of PMMA has engendered a search for alternative materials that have sufficient oxygen permeability. In order to meet the oxygen transmission requirement, a wide variety of polymers have been investigated from polyhydroxyethyl methacrylate hydrogel to siloxane- and fluorosiloxane-containing hydrogels.2 The quest for optimal polymeric materials was soon followed by an early concept of the smart contact lens, which involved incorporation of a drug-delivery system and an intraocular pressure sensor for glaucoma diagnosis within the lens.

In this issue of ACS Nano, Hong and colleagues demonstrated extended function of the smart contact lens by coating one side of a hydrogel lens with graphene to protect the eyeball from both electromagnetic (EM) wave damage and dehydration discomfort.3 Graphene’s remarkable electrical, mechanical, and chemical properties have called for a reliable and efficient synthesis route, and today, chemical vapor deposition (CVD) is the most common method of supplying graphene for various applications.4 In particular, graphene’s...
densely packed, hexagonal lattice made of carbon atoms, which prevents water penetration across the graphene film, has led to its potential use as eye protection from dehydration. Although graphene is nearly transparent optically, its optical thickness often enlarges for EM waves in the MHz and GHz ranges. Along with high electrical and thermal conductivities, these features of graphene promise immediate adaptability to the smart contact lens.

In this Perspective, we provide a brief overview on and describe prospects of feasible functions of graphene for smart contact lenses. Outstanding electrical properties such as low sheet resistance and considerable charge carrier mobility enable graphene’s use in transparent electrodes and fast-response sensors, suitable components for a wearable device. Interactions between external magnetic fields and electrons in graphene help to shield EM waves in certain frequency ranges. Due to the mass impermeability of the pristine graphene lattice, graphene can mitigate ocular dehydration. Finally, in order to adjust near- and far-sightedness, graphene can change the focal length of a polymeric soft contact lens.

Metal electrodes are an essential component of electronic devices and provide desired electrical properties; for wearable devices, however, their use could be limited by mechanical failure and opacity if future wearable electronics, including the smart contact lens, demand more flexibility, stretchability, and transparency. Especially for the smart contact lens, the relatively bulky film of the metal electrode can be constrained for issues in biocompatibility, corrosion, and oxygen permeation, thereby hampering daily wear. Ever since the CVD on Cu foil graphene synthesis method was developed in 2009, graphene has been intensively considered as a potential alternative to metal electrodes and transparent indium—tin—oxide electrodes. Having lots of grain boundaries, CVD-grown graphene with Young’s modulus of 1 TPa and spring constant of 1–5 N/m is as strong as mechanically exfoliated graphene, the first isolated type of graphene. These values are among the best mechanical properties measured so far, enabling graphene transfer onto flexible and rough surfaces. Low and uniform sheet resistance of 250 Ω/sq measured over 400 × 300 mm² of graphene is on a par with those of the transparent electrodes. Interestingly, graphene sheet resistance is invariant in stretching (<12%) and tensile strength (<6.5%), evidenced by the complete recovery of the electrical property. One-atom-thick graphene is rather transparent, adsorbing only 2.3% of incident light in the entire ultraviolet—visible—infra-red wavelength range. These unique characteristics enable researchers to delve into electronics applications ranging from flexible electronics and organic light-emitting diodes (LEDs) to energy devices and wearable electronics.

As described in this issue of **ACS Nano**, Hong and colleagues were interested in utilizing graphene as a multifunctional film material on a soft contact lens substrate. The concept of the graphene-based smart contact lens can be justified if considering the feasibility of miniaturized and thinner circuitry, electrical characteristics, mechanical stability, and transparency. For example, CVD-grown graphene is not only semimetallic, with in-plane sheet resistance as low as 593 Ω/sq, but also able to lie on a flexible surface like a lens. Hybrid design of graphene and silver nanowires can further decrease sheet resistance of 30 Ω/sq at the expense of transparency (94%).

The large specific surface area of 2630 m²/g, which enables facile functionalization, adds to the advantages of graphene for the smart contact lens. The unique band structure of pristine graphene further enables it to respond and to sense quickly. Based on these benefits, graphene functionalized with glucose oxidase can selectively respond to glucose. If utilizing the charge-neutral-point shift phenomenon, a field-effect transistor out of the functionalized graphene can detect a glucose level in the range of 3.3–10.9 mM that brackets most of the reference range of medical examination or screen test for the diagnosis of diabetes. Monitoring glucose levels from tears could accurately approximate bloodstream glucose levels, given that the tear film is closely associated with blood across a tear—blood barrier.
The tear film, which is composed of three layers, plays important roles in cleaning up and lubricating the eyes as well as in providing clear vision.1 Dehydration of the eyes, called keratoconjunctivitis sicca, or dry eye syndrome, can occur when tears either are no longer produced or they evaporate quickly. If left untreated, dry eye syndrome can bring about severe complications including impaired vision or loss of sight.

The gastight lattice of CVD-grown graphene could prevent dry eye syndrome by inhibiting excessive evaporation of tears. In fact, mechanically exfoliated, pristine graphene is impermeable against gases including helium. Water vapor transmission of CVD-grown, large-scale graphene is as negligibly small as $10^{-4}$ g/m$^2$·day for the first few hours with high transparency and mechanical stability kept unaltered.5,13 Thus, CVD-grown graphene can keep the hydrogel contact lens hydrated, although graphene does not cover the eyes directly. Otherwise, if the lens is dehydrated, the tear film on the eye dwindles away, oxygen permeation decreases, and the contact lens refractive index increases. Hong and colleagues report water vapor transmission rates to be 0.1181 g/cm$^2$ per day for a hydrogel soft lens and 0.0791 g/cm$^2$ per day for a graphene-covered soft lens after a 7 day long measurement (Figure 3a). The 30% decrease in the water vapor transmission rate is attributable to a screening effect of the graphene-coated contact lens.

The ability for a single lens to be multifocal is another fascinating feature that adds to the promising advantages of graphene-incorporated smart contact lenses. As people grow older, they inevitably develop a symptom called presbyopia, which leads to difficulty in focusing on near objects. There are two types of state-of-the-art multifocal lenses. One design, called an alternative design, is similar to bifocal glasses and is composed of two zones in a contact lens for distant vision at the center and near vision at the edge of the lens; the other design, called a simultaneous design, has both portions for distant and near visions in front of the pupil. With the electrically induced deformation behavior of dielectric elastomers, research on using deformable membranes as optical lenses is ongoing to enable the active membrane to change its curvature reversibly from flat to a concave or convex shape under an electrical bias. Recently, a transparent actuator integrated with chemically exfoliated graphene film has been demonstrated.14 In order to achieve the electro-deformation behavior of the lens, both transparent elastomers and conductive materials are needed.15 Reported values of the sheet resistance of the graphene are as low as 0.45 kΩ/sq, which is comparable to those of CVD-grown graphene. Depending on voltage and frequency, the electro-displacement of the elastomer can vary from 29 to 946 μm with optical transparency of 57%. Even though high voltage is still needed to bend the elastomer, the focal length change reported in the literature offers the potential to use graphene for the multifocal lens component.

PROSPECTS

Google’s invention of the smart contact lens for sensing glucose in tears has garnered worldwide interest in wearable electronics. The idea of a lens equipped with a tiny display and a camera that can project images into the user’s own field of vision is being pursued by other market leaders such as Samsung and Sony. In the speedy course of this development, there are a few research topics that deserve attention. Oxygen permeation can be ranked high on the list. Because permeance is inversely proportional to thickness, the three-layer (lens, circuitry, and protective coating) structure of smart contact lenses that has been validated thus far could cause such hypoxia-related complications as red eyes and corneal neovascularization. If graphene takes the place of the circuit layer, the mass impermeability of graphene may impede oxygen accessibility to the cornea. Nevertheless, this potential risk might be addressed by use of nanoporous graphene membranes.16 Figure 3b illustrates the possible pathway of oxygen across a nanoporous graphene layer that we characterized and a hydrogel contact lens from suppliers. As the oxygen molecules travel to the eyeball, they would encounter two resistances, from the nanoporous graphene and from the polymer contact lens. Because the oxygen permeance of the nanoporous graphene is greater than that of the contact lens by many orders of magnitude, the permeation resistance, $R_NPG$, coming from the nanoporous graphene becomes negligible.17 Therefore, without the concern of hypoxia, nanoporous graphene can help embed ultrathin circuitry within the smart contact lens. Loss of tears by water evaporation could be controlled by engineering the pore sizes of the nanoporous graphene. In this way, the cornea can be exposed to a clinically safe amount of oxygen and be protected from anoxia-level dehydration. However, the successful utilization of nanoporous graphene in smart contact lenses depends critically on the establishment of synthesis options at large and intermediate scales.

Figure 3. (a) Relative water vapor transmission rate (WVTR) of graphene showing the dependence on the polymer substrate and the number of layers. The red bar shows the relative WVTR of monolayer graphene on hydrogel contact lenses (bioxifilon A). Black bars show how relative WVTR of graphene on a polyethylene terephthalate (PET) substrate changes with layer number. All the bars are normalized by WVTR of each polymer substrate. (b) Schematic of oxygen penetration through nanoporous graphene and hydrogel contact lenses. $P_i$, $P_o$, and $P_h$ are the external, interlayer, and internal pressures, respectively. $R_{NPG}$ and $R_{HG}$ are permeation resistances of graphene and hydrogel, respectively. (Inset) Oxygen permeances for various contact lens materials (supplier data) and porous graphene (authors’ characterization). A black dotted line indicates a desirable oxygen permeance level to avoid hypoxia-related complications such as for corneal anoxia with extended (or overnight) wear for closed eye conditions.21
With advances in the Internet of Things technologies, use of EM waves in the MHz and GHz ranges can result in a deleterious effect on eyes as Hong and colleagues hinted in their article, noting that egg white underneath a normal soft contact lens was damaged in a microwave oven. Although they showed that the use of a graphene contact lens could counterbalance this effect, another concern arises that dissipated heat over the graphene contact lens can augment tear evaporation. In order to avoid these EM-wave-related effects, sustainable and renewable power sources with no side effect are highly desired. Here, there are opportunities for two-dimensional (2D) materials. Osmotic power generation, also called blue energy, is conceivable if a nanoporous 2D layer of MoS2 can, for example, maintain the salt concentration difference across itself. Using both the salt gradient and the ultranarrow 2D solid-state pore, this nanogenerator could produce a large current osmotically, potentially with great power density. Evaporating tears from the eyes could build up an osmotic pressure gradient across the contact lens to generate power. When an eyeball is under strain from looking around, another concern arises that can deleterious effects on eyes as Hong and colleagues hinted in their article, noting that egg white underneath a normal soft contact lens was damaged in a microwave oven. Although they showed that the use of a graphene contact lens could counterbalance this effect, another concern arises that dissipated heat over the graphene contact lens can augment tear evaporation. In order to avoid these EM-wave-related concerns, sustainable and renewable power sources with no side effect are highly desired. Here, there are opportunities for two-dimensional (2D) materials. Osmotic power generation, also called blue energy, is conceivable if a nanoporous 2D layer of MoS2 can, for example, maintain the salt concentration difference across itself. Using both the salt gradient and the ultranarrow 2D solid-state pore, this nanogenerator could produce a large current osmotically, potentially with great power density. Evaporating tears from the eyes could build up an osmotic pressure gradient across the contact lens to generate a small yet sufficient current to power the smart contact lens. In addition to the osmotic power generator, piezoelectricity of the 2D MoS2 could lead to a piezoelectric nanogenerator of power when an eyeball is under strain from looking around. In addition, the aforementioned graphene could feasibly be a main component of transparent, flexible triboelectric nanogenerators.

In order to adapt graphene to practical applications, the first common issue to address is the underdeveloped methods for the scale-up and continuous production of graphene. In the future, smart contact lenses could be widely used to monitor and to diagnose diseases continuously. If equipped with actuator functions, they could also be adapted in therapeutics such as an ocular drug-delivery platforms. Furthermore, lenses equipped with a display application will be able to provide augmented reality as the on-demand information will be projected directly in the field of view.

AUTHOR INFORMATION

Corresponding Author
*E-mail: parkh@ethz.ch.

ORCID

Hyung Gyu Park: 0000-0001-8121-2344

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support from Commissions for Technology and Innovation (CTI), Federal Department of Economic Affairs, Education and Research (EAER), Switzerland (KTI-Nr. 18463.1 PFEN-MN). Christina Sauter (ETH Zurich) characterized the oxygen permeance across porous graphene, which we appreciate.

REFERENCES