

ORGANIC LIGHT-EMITTING DIODES

Non-oxide boost

Researchers have shown that organic light-emitting diodes with transparent graphene electrodes are more flexible and exhibit higher efficiencies than those whose electrodes are made from rigid indium tin oxide.

Yu Zhu and James M. Tour

Most electrodes in today's organic light-emitting diodes (OLEDs) are made from indium tin oxide (ITO), a transparent conducting oxide. It is commonly thought that all OLEDs are bendable, owing to the flexibility of their organic constituents. However, this is not entirely true, as the ITO forming the transparent electrodes is a brittle oxide.

Reporting in *Nature Photonics*, Tae-Hee Han and colleagues from Pohang University of Science and Technology, Sungkyunkwan University and Seoul National University in Korea demonstrate that OLEDs fabricated with graphene transparent electrodes are not only flexible but also more efficient than OLEDs whose electrodes are based on ITO. This work highlights the use of graphene for applications in the construction of advanced electronic devices¹.

Conducting polymers, carbon nanotubes and graphene-based transparent electrodes have all been explored as alternatives to ITO for use in flexible OLEDs. Although these transparent materials exhibit better flexibility than ITO, OLEDs employing these materials have poorer performance than devices fabricated from ITO-coated poly(ethylene terephthalate) (PET), the substrate commonly used in flexible electronics. Therefore, despite its inflexibility², ITO remains the most popular material for use as transparent electrodes, even for electronic devices that are claimed to be 'flexible'.

The conductivity of an electrode material is a major factor in determining its efficiency. The typical sheet resistance of ITO is in the range of 10–100 $\Omega \square^{-1}$, whereas carbon nanotubes and conductive polymers typically reach 100–1,000 $\Omega \square^{-1}$ at the same transmittance^{3,4}. Recent advances^{5,6} in graphene synthesis have led to breakthrough sheet resistances of around 30 $\Omega \square^{-1}$ at 90% transmittance — a value that surpasses that of ITO in some cases. However, the direct use of graphene in OLEDs does not result in an immediate efficiency boost.

Han and colleagues found that a high work function is an equally important factor for achieving high-efficiency OLEDs with transparent graphene electrodes¹.

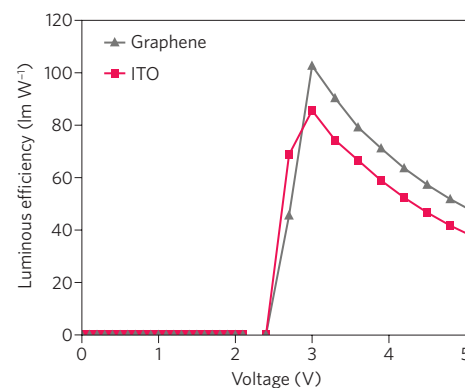
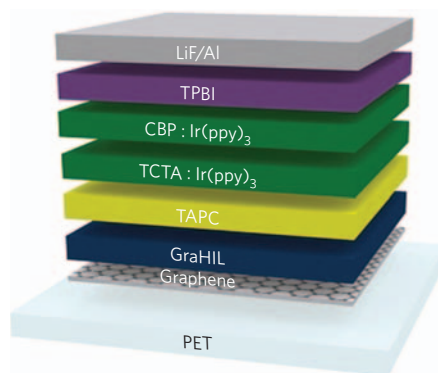


Figure 1 | Left, phosphorescent OLED device whose graphene anode has been modified with a gradient hole injection layer (GraHIL). Right, a comparison between the luminous efficiencies of phosphorescent OLEDs based on graphene and ITO electrodes. TPBI, 1,3,5-tri(phenyl-2-benzimidazolyl)-benzene; CBP, 4,4'-N,N'-dicarbazolylbiphenyl; TCTA, 4,4',4''-tris(carbazol-9-yl)-triphenylamine.

Graphene usually serves as the anode in OLED devices (Fig. 1, left), but with the relatively low work function of around 4.4 eV. Compared with the ionization potentials of common hole transport layers such as *N,N'*-bis(naphthalen-1-yl)-*N,N'*-bis(phenyl)benzidine (NPB) or 1,1'-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), which are around 5.4 eV, graphene's low work function causes an unfavourably high injection barrier at the interface that lowers the current efficiency of the final device.

Hans and colleagues adopted two elegant procedures to adjust the conductivity and work function¹. First, they looked for graphene with the lowest sheet resistance hitherto recorded. Pristine synthesized graphene typically has a sheet resistance of around 1,000 $\Omega \square^{-1}$, and the resulting high operating voltage limits the luminous efficiency of the final device. By collaborating with top graphene synthesis groups⁵, Hans and colleagues fabricated four-layer graphene transparent electrodes with sheet resistances of around 34 $\Omega \square^{-1}$ at 90% transmittance — a value that rivals commercially available ITO electrodes. Second, to ensure a high work function, the team employed a well-engineered conducting polymer whose work function could be tuned to improve hole injection from the graphene anode to the organic layer (Fig. 1,

right). The conducting polymer, which the researchers refer to as the gradient hole injection layer (GraHIL), comprises poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulphonate) (PEDOT:PSS) and a tetrafluoroethylene-perfluoro-3,6-dioxo-4-methyl-7-octenesulfonic acid copolymer (a perfluorinated ionomer). This conducting polymer provides a work function gradient across the layer and a relatively high surface work function of 5.95 eV, which allows the holes to be injected efficiently into the overlying hole transport layer.

These improvements in conductivity and work function significantly enhanced the performance of the final devices, even to a point that rivals state-of-the-art rigid ITO-based OLEDs⁷. Specifically, the researchers demonstrated that green fluorescent and phosphorescent OLED devices utilizing such four-layer HNO₃-doped graphene anodes exhibited luminous efficiencies of 37.2 lm W⁻¹ and 102.7 lm W⁻¹, respectively. These values are significantly higher than those of optimized devices exploiting ITO-based electrodes, which achieve efficiencies of 24.1 lm W⁻¹ for fluorescent OLEDs and 85.6 lm W⁻¹ for phosphorescent OLEDs. The researchers also showed that a flexible fluorescent white OLED with a four-layer HNO₃-doped graphene anode exhibits a current efficiency of around 16.3 cd A⁻¹,

which is higher than that of ITO-based OLEDs (10.9 cd A^{-1}).

This is the first time that an OLED with non-oxide transparent electrodes has exhibited better fluorescent and phosphorescent efficiencies than one based on ITO, which suggests that this alternative transparent electrode could compete with commercial ITO in terms of performance. Doping graphene and introducing a well-engineered work-function-tunable hole injection layer are both crucial steps for achieving such high efficiencies in a graphene-based OLED. The major limitation of this work is that the stability of these new materials has not been well-investigated. For example, although pristine graphene is very stable under ambient conditions, the acid dopant used in the white OLED could gradually migrate out of the system,

thereby increasing the sheet resistance and degrading the surrounding acid-sensitive electronics. Another concern could be the fabrication and processing cost of start-of-the-art graphene, which is synthesized through a chemical vapour deposition method on high-purity metal foil substrates. Despite such limitations, this work will certainly encourage the development of cost-effective techniques for synthesizing graphene with enhanced pristine conductivity, particularly now that successful application-level prototype devices have been demonstrated. The flexibility and high efficiency offered by graphene will provide engineers with a powerful tool for designing new generations of consumer electronics. The promise of graphene in state-of-the-art electronics is now one step closer to reality. □

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References

1. Han, T.-H. *et al. Nature Photon.* **6**, 105–110 (2012).
2. Cairns, D. R. *et al. Appl. Phys. Lett.* **76**, 1425–1427 (2000).
3. Geng, H.-Z. *et al. J. Am. Chem. Soc.* **129**, 7758–7759 (2007).
4. <http://www.clevios.com>
5. Bae, S. *et al. Nature Nanotechnol.* **5**, 574–578 (2010).
6. Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. *Nature Photon.* **4**, 611–622 (2010).
7. Helander, M. G. *et al. Science* **332**, 944–947 (2011).

LASER PHYSICS

All-atom parametric oscillator

By using a one-dimensional optical lattice to control and confine the location of cold ^{87}Rb atoms, researchers have created a distributed Bragg reflector that enables optical parametric oscillation solely from atoms.

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The standard picture of a laser or optical parametric oscillator comprises a gain medium between two mirrors, which together form an optical cavity. Steady-state oscillation of the output optical field is achieved when the gain equals the round-trip optical loss within the cavity. Historically, the first lasers were constructed using gain media that relied on optically active centres in solid-state crystals (such as chromium ions in a ruby crystal) or room-temperature gases of atoms (such as mixtures of helium and neon). Although a pair of parallel end mirrors is the most straightforward way of creating an optical cavity, optical feedback can also originate from the spatial structure of the medium through which the light propagates — a class of lasers known as distributed feedback (DFB) lasers. A one-dimensional periodic patterning of the medium's refractive index creates a resonant scattering (Bragg scattering) condition at a particular wavelength and angle. The strength of this feedback depends on the number of periods as well as the strength of the refractive index modulation. If the feedback and gain are strong enough, lasing can occur without the use of conventional mirrors. This interesting type of lasing is popular for use in semiconductor systems, where the gain medium can be easily

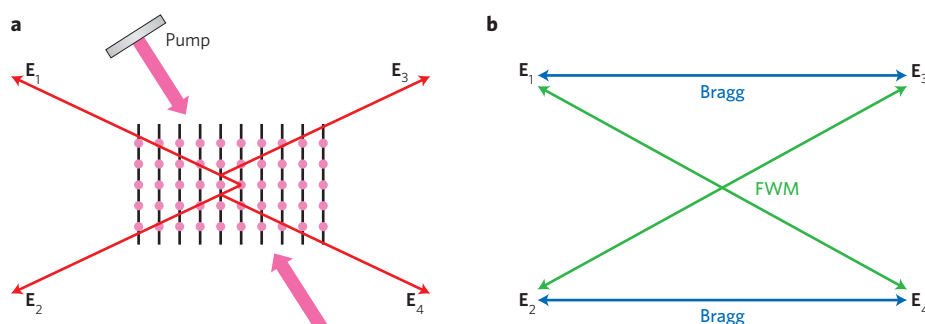


Figure 1 | Optical parametric oscillation with distributed feedback in cold atoms. **a**, Atoms are cooled and trapped in a one-dimensional optical lattice, where they provide resonant optical feedback (Bragg scattering) for light travelling at a specific angle with respect to the lattice axis. Light is generated along these directions by the atomic cloud through the FWM of two counter-propagating pump beams. **b**, Feedback diagram showing how Bragg scattering and FWM couple the four output fields. The output fields can reach stable oscillation if the gain from FWM is above a threshold value.

grown or etched at periodic intervals. Such semiconductor DFB lasers are standard commercial products that play an important role as high-performance transmitters in telecommunications systems.

Writing in *Nature Photonics*, Alexander Schilke and co-workers have now extended the concept of DFB lasing to systems in which gas-phase atoms are the gain medium. Of course, atomic media have

been used in lasers for the past half-century, but the implementation of distributed feedback within them has been difficult for several reasons. First, the real part of the index of refraction for a single atom such as ^{87}Rb only differs from the vacuum near an optical transition, where there is significant absorption owing to the imaginary part of the index. This difference is very small, so a large number of atoms and a near-resonant field