



P-Ink and Elast-Ink from lab to market

A notable trend these days amongst academics is the increasing tendency to transfer the fruits of their research to the marketplace through a large number of spin-off companies, all racing to develop, manufacture, and commercialize products. In this article we present a personal account of some of our recent research in the area of photonic crystals that over the course of the last five years has evolved from a laboratory curiosity to a commercializable technology. Two of these nanotechnology platforms, termed P-Ink and Elast-Ink, are both founded on active color tuning of opals, a capability that provides electrical and mechanical access to materials with any visible color, as well as invisible near-infrared and ultraviolet wavelengths. These actively tuned opals show considerable promise for new-generation full-color displays, surface coatings, biometric security and authentication devices.

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Where it all began

Since the announcement a decade ago by Sajeev John¹ in the Physics Department at the University of Toronto that 'silicon inverse opal' could theoretically display a complete photonic bandgap at optical telecoms wavelengths, followed soon after by the first self-assembly synthesis of silicon inverse opal, and confirmation, by our research group², of John's predictions, many scientists have imagined the future of this fascinating new class of materials as 'semiconductors for light'. The large-scale synthesis of

Si inverse opal inspired dreams of a world where 'semiconductors for electrons' enabled by electronic bandgaps might be challenged, and 'semiconductors of light' would enable impressive feats in optical telecoms and computing³⁻⁶.

In the years that followed, the initial burst of enthusiasm about 'self-assembling optical chips' has been considerably dampened, since most of the promises of opal-based photonic bandgap materials were contingent on the creation of opals with an absolutely perfect structure. This extremely high degree of structural perfection is

almost impossible to achieve in opals by self-assembly because of the pervasive occurrence of intrinsic defects, such as sphere size variations, and vacancies, as well as lattice stacking faults, dislocations and microcracks⁷. Imperfections in photonic crystals cause light loss through multiple scattering of the light at defects – something that optical engineers have an aversion to when designing and building optical devices for optical telecoms. A few years ago we justifiably wondered whether or not the end of the road for opals was in sight.

Since that time a wealth of new opportunities for opals that are 'defect tolerant' have presented themselves. They all revolve around the principle that humans perceive color with a spatial resolution of around $100\ \mu\text{m} \times 100\ \mu\text{m}$, a typical size for pixels in digital photographs, printing, and displays. We reasoned that, as far as the human eye is concerned, light reflected from opals would appear bright and colorful because the imperfections are much smaller than can be perceived by humans: hence perception of color from opal structures is forgiving of defects. Furthermore, one only requires about ten unit cells covering an area of a few microns, much smaller than the eye can see, for an opal to show off its full iridescence. Based on this realization, two exciting opportunities presented themselves, centered on 'structural color' of passive and active opals. The former offers static, permanent and non-reversible color products, while the latter provides dynamic, changeable, reversible color devices.

We began to imagine passive opal color as a new kind of pigment, which could be creatively integrated into jewelry and clothing, paint and cosmetics, print and artwork, vehicles and buildings, to provide them with customized hues and colourful visual effects. Moreover, the ability to create active opal color, and hence tunability using

chemical and physical stimuli, would greatly multiply the opportunities for these types of materials. For instance, opal color, sensitive to particular molecules, opens the door to chemical and biochemical sensors⁸, electrically tuneable opal color shows the way to full-color coatings⁹, and mechanically actuated opal color provides an inroad to security systems¹⁰. Just imagine high-rise buildings that adjust their color throughout the day, vehicles that adapt their color to their surroundings, full-color outdoor billboards that are refreshed on demand, and anticounterfeit devices that challenge the best forgers. With the impressive compositional versatility of opals, the possibilities for colored opal products are truly boundless.

This article is a personal account of two opal opportunities that began as laboratory curiosities and ended as technologies poised for the marketplace^{9,10}. They are both founded on active color tuning of opals. One is made of a metallopolymer opal gel that reversibly swells and shrinks with application and removal of a voltage. The other is made of an elastomeric opal that undergoes reversible dimensional changes on applying and removing a mechanical force.

The underlying principle behind these devices is some simple opal optical geometry (Fig. 1), which after a little mathematics gives rise to the Bragg–Snell equation shown below. This allows one to appreciate the origin of the wavelength of the reflected light and the way to achieve passive and active structural color:

$$\lambda = 2D(n_{\text{eff}}^2 - \cos^2\theta)^{1/2} \quad (1)$$

In the Bragg–Snell equation, λ is the wavelength of reflected or transmitted light; n_{eff} is the volume-weighted average of the refractive

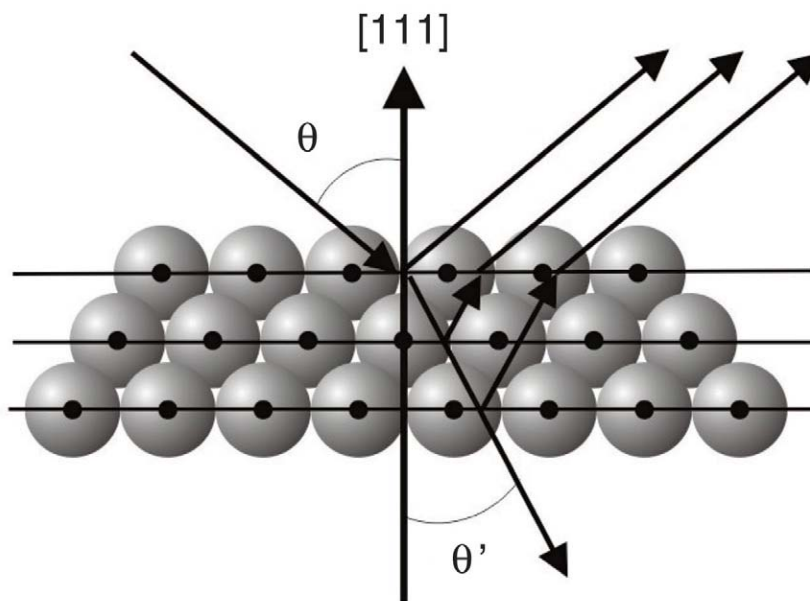


Fig. 1 Geometrical optics for light incident on the {111} crystal plane of an opal at an angle θ which undergoes refraction and diffraction to give structural color that can be seen in reflection or transmission.

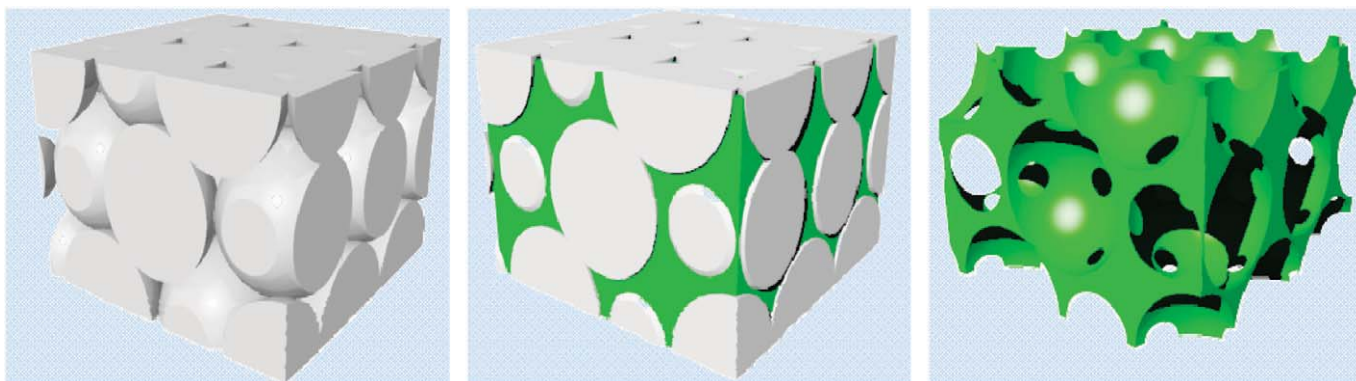


Fig. 2 Graphical illustration of the process of chemically transforming an opal (left) into a composite opal (middle) where the spheres and infiltrated material are colored white and green, respectively, and finally an inverse opal (right) where the spheres have been etched away, leaving behind the replica material.

index of the constituent opal spheres and whatever occupies the interstitial voids, $n_{\text{eff}} = (0.74n_{\text{sphere}} + 0.26n_{\text{void}})$; D is the distance between the {111} lattice planes given by $D = \sqrt{(2/3)d}$, where d is the diameter of a sphere; and θ is the Bragg angle of incidence of the light falling on the opal. Passive structural color originates from opals in which sphere sizes and effective refractive index are fixed; tuning one or both of these parameters yields active structural color. Opals comprise a colloidal assembly of spheres with diameters most often in the range of 100–1000 nm¹¹. Given a chance, these spheres will prefer to crystallize in a face-centered cubic lattice with the {111} crystal plane oriented parallel to the underlying substrate, as shown in Fig. 1. In this opal configuration, light is incident on the {111} crystal face at an angle θ and undergoes refraction then diffraction to produce structural color that can be observed by reflection or transmission¹².

As mentioned above, it is easy to appreciate that an opal will give Bragg diffraction of a single color whose wavelength is predicated on the choice of sphere size and effective refractive index of the sphere–void composite. The most common materials for making spheres with size uniformity better than the 5% needed for well-ordered opal formation are silica and polystyrene¹³. Static color can be manipulated by changing the composition of the spheres or inverting the opal to an inverse opal. The former is not so easy to do because of the challenge of synthesizing spheres of a uniform size and controlling the surface potential to enable them to undergo colloidal assembly to form a well-ordered opal. However, some promising developments have been reported in this area of opal research¹³. The latter is easier to achieve through replication of the opal in a material of choice (Fig. 2).

The color shift caused by going from the opal to the inverse opal stems from the fact that spheres have become voids, and voids are now material; the effective refractive index is therefore given by $n_{\text{eff}} = (0.74n_{\text{void}} + 0.26n_{\text{material}})$ instead. In the case of opal composite the effective refractive index is rather $n_{\text{eff}} = (0.74n_{\text{sphere}} + 0.26n_{\text{material}})$.

The way to active opal color is thus clear: all that one needs to do is identify opal-based materials whose lattice dimension and/or effective refractive index can be continuously tuned through the application

of a stimulus. The opal will respond by providing a range of colors. Currently, no other single material is capable of performing this feat. Actively tuned opals represent a new class of materials where a single opal material gives a range of visible colors, as well as the invisible ultraviolet and near-infrared spectral range.

This is the background to our account of how two classes of color-tunable opals, P-Ink and Elast-Ink, were invented in our group and led to the foundation of a new company, Opalux, to take active opal color materials from lab to market.

Electrically and mechanically tunable opals

Photonic Ink, or P-Ink⁹, is a composite comprising an opal embedded in a matrix of a specialized redox-active polyferrocenylsilane gel. When this metallopolymer gel is incorporated into an electrochemical cell, varying the applied voltage causes the gel to swell and shrink reversibly, and concomitantly the color of the P-Ink material can be shifted as depicted in Fig. 3. In this way, we demonstrated for the first time an electrically driven device whose color could be shifted to any wavelength across the whole visible spectrum. It was obvious from these results that this technology could form the basis of full-color opal coatings for a wide range of applications.

The second technology, an elastomeric inverse opal dubbed Elast-Ink¹⁰, also with promising market potential, is responsive to mechanical pressure. This material is made by combining opal with synthetic rubber to form a composite opal and subsequently dissolving away the opal to leave an interconnected network of air voids embedded in a rubbery matrix, as shown in Fig. 4. The elastic inverse opal, because of its highly porous architecture, can be easily compressed, and its color gradually shifts across the entire visible spectrum as increasing pressure is applied. Using this system we have demonstrated a highly sensitive and accurate fingerprint sensor, wherein the elastic inverse opal captures in full color the topography of the ridges and valleys on a person's finger. With potential applications in forensics, biometrics, security and authentication devices, this material could provide viable solutions to an increasingly security-conscious world.

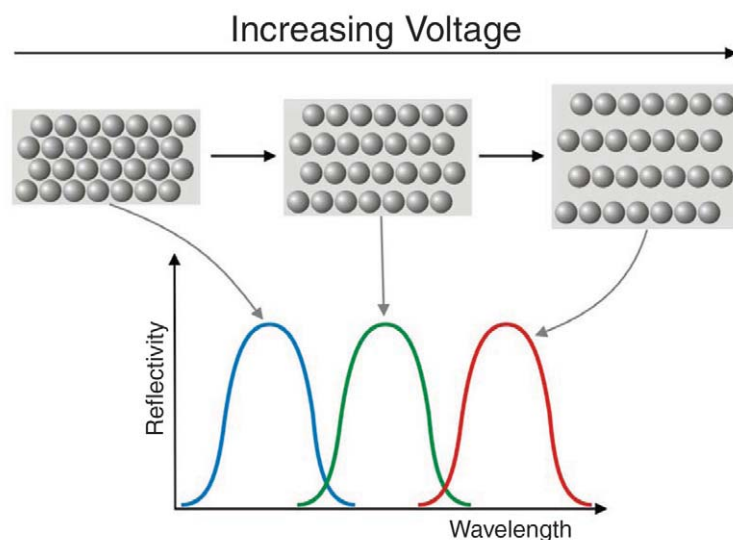


Fig. 3 Illustration of the operation of P-Ink voltage-tunable full-color opal coatings.

It was clear to us that the P-Ink and Elast-Ink platforms could form the basis of new products in diverse markets. The intrinsic advantages of these technologies offered clear commercial possibilities, and so Opalux was founded as a Toronto-based company in 2006. The mandate of Opalux is to develop and commercialize opal-based products, with a particular emphasis on P-Ink and Elast-Ink technologies.

P-Ink

As mentioned above, P-Ink is an opal-based technology that provides electrically tunable color of any wavelength. By coating this material onto an array of pixels, a full-color display can be created wherein the color of each pixel can be varied at will (Fig. 5). Since this technology is reflective, it works exceedingly well in bright sunlight, where other

emissive display technologies, such as liquid crystal, plasma and light-emitting diode, are overwhelmed by glare.

Given its performance, we believe this technology could certainly address the needs of the multibillion-dollar market for outdoor advertising billboards, and could be incorporated into large, bright, paper-like billboards whose content could be changed electronically, like a television screen. In 2005, advertisers spent US\$6.3bn in the US market alone, with a yearly growth of nearly 10% (Outdoor Advertising Association of America, www.oaaa.org).

As might be expected, during the development of the P-Ink technology, a great number of technical challenges had to be overcome. Amongst these was the initial screening and identification of an air- and humidity-stable, voltage-tunable polyferrocenylsilane, whose synthesis was scalable to kilograms. The one proven to be

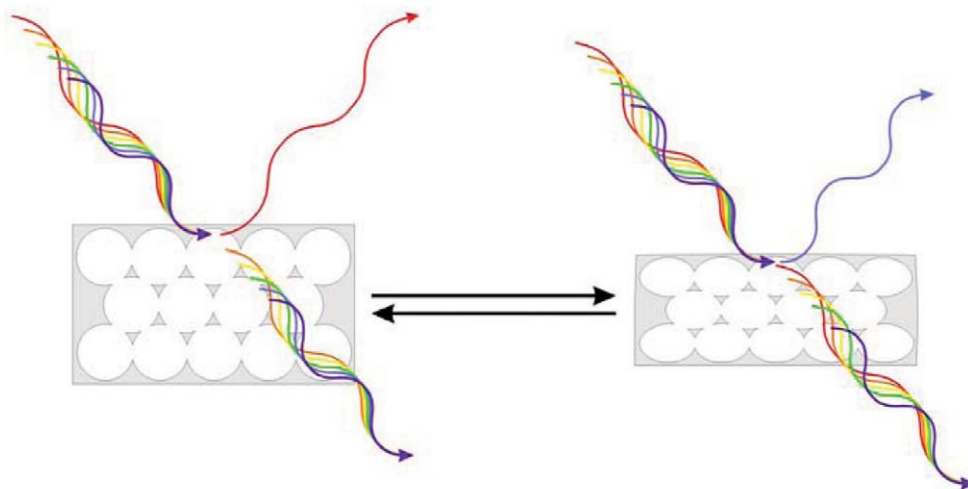


Fig. 4 Elastic inverse opal, Elast-Ink, where compression reduces the lattice constant and blue-shifts the color.

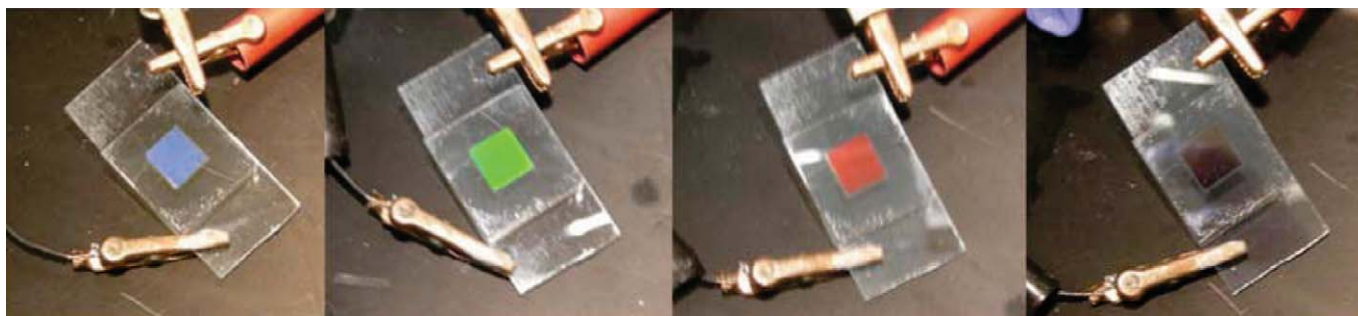


Fig. 5 Switching of a P-Ink pixel in response to a voltage increasing from left to right.

most suitable is a controlled molecular weight polyferrocenylsilane incorporating pendant C=C double bonds⁹. It can be crosslinked through a convenient thiol-ene reaction to make it function as a voltage-activated swellable/shrinkable polymer gel.

Another hurdle that had to be surmounted was the incorporation of this redox-active metallopolymer gel into an opal without an overlayer, to avoid interfering optical and mechanical effects. It was also important to form strong substrate-sphere bonds, to create a

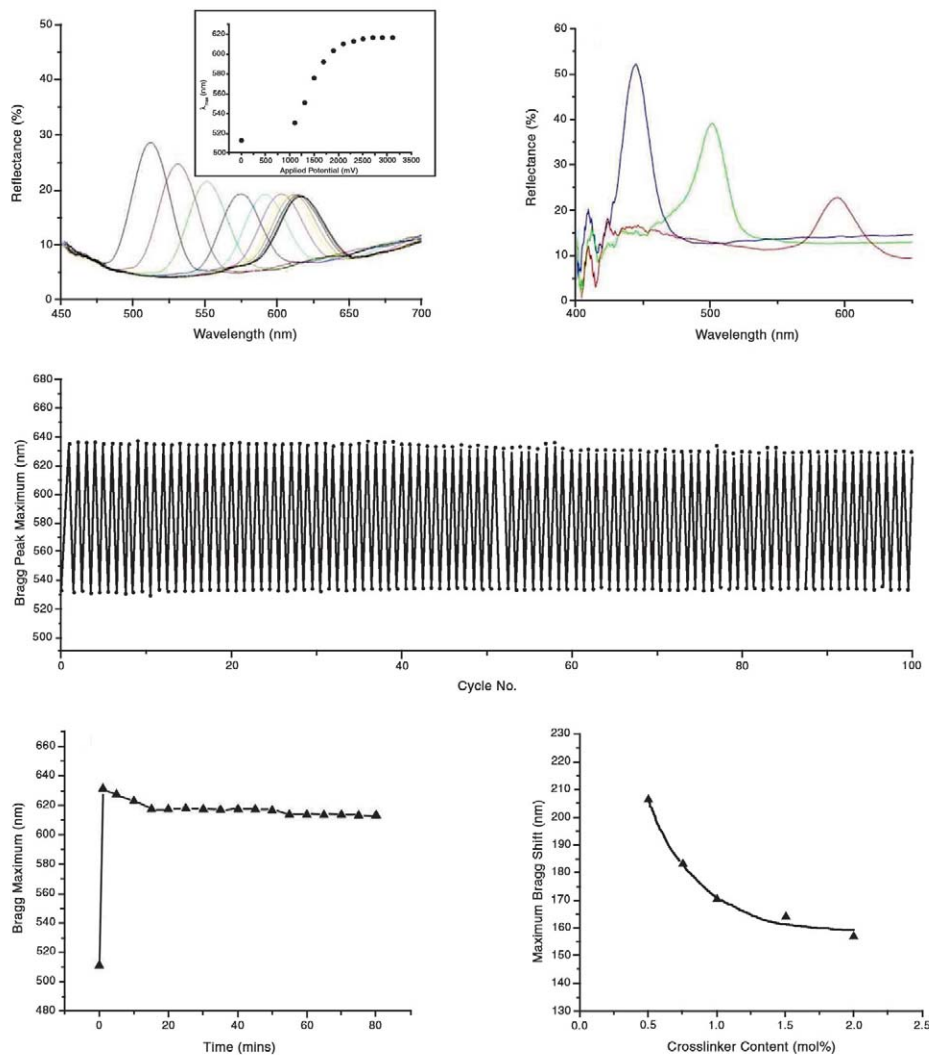


Fig. 6 P-Ink electromechanochromic performance. (a) Reflection spectra at increasing voltage. Inset shows dependence of the peak position on applied voltage, showing a continuum of accessible colors. (b) Spectra showing reflection of all three primary colors upon increasing voltage incrementally. (c) Bragg peak maximum for 100 redox cycles. (d) Electrical bistability demonstration. (e) Cross-link density control of maximum tuning range.

mechanically stable functioning device, which could be electrically cycled many times without chemical, photochemical or mechanical degradation.

It was also necessary to develop proprietary large-scale opal film-forming methods that were compatible with an industrial-scale and low-cost production process. Prototype full-color pixelated P-Ink devices have been demonstrated; examples of achievable colors are shown in Fig. 5. Furthermore, P-Ink displays bistability associated with stable oxidized and reduced forms of the metallopolymer, which means that an image can be maintained without applying power, a great boon for saving energy and battery life. And finally, P-Ink can be grown on curved surfaces and integrated onto flexible substrates to enable photonic paper, a potential competitor to the electronic paper being developed by E-Ink, Kent and MagInk. Note that E-Ink technology (www.eink.com) is based on electrophoretic switching between reflective black and white halves of microspheres, whilst Kent (www.kentdisplays.com) and MagInk technology (www.magink.com) works via electric field switching of diffracting cholesteric liquid crystals. In these systems full color is obtained by color filters or mixing of primary colors.

What is left to be done?

Before P-Ink products can go to market a significant amount of research still needs to be performed. Materials characteristics must be honed to control color-switching times, wavelength-tuning range and mechanical strength. Already color tuning from the blue to the infrared has been achieved, over several hundred cycles, and with color-changing times in the sub-second range (Fig. 6). The thickness and refractive index contrast of P-Ink have to be refined to boost the reflection intensity, and creative schemes have to be formulated to gain command over the hue, saturation, lightness and angle dependence of reflected colors. The power requirements to drive P-Ink are already impressively low with voltages and currents below

1.5 V and 100 mA, respectively, but can probably be further improved by manipulating the electrical conductivity of the polymer and the ionic conductivity of the electrolyte. In addition, various kinds of modifications to the device architecture are being used to reduce the switching times hopefully to video rates and increase the size of P-Ink cells. Already pixel sizes of several square inches have been demonstrated to work. A number of short- to long-term stability tests are under active investigation, including electrical, ultraviolet light, heat-cold, shock resistance, and a host of other industry-standard tests. No one said it was going to be easy to start a new company to produce a completely new full-color display!

Does P-Ink have a future?

In the outdoor signage market there is a scarcity of products currently available that allow for changeable content. As mentioned before, most of the existing devices use emissive technologies, which are poorly visible in bright sunlight. While a number of reflective display technologies are being developed, most are not suited to large displays because of the intricacies involved in manufacture and assembly. The only company currently producing outdoor signage based on a reflective technology is MagInk mentioned above. While MagInk's technology is very interesting and has great potential, it holds only a miniscule market share, meaning that the market is effectively wide open for a competitive alternative, such as P-Ink. In addition, there is a long list of potential non-display markets where P-Ink could find a ready home. Color-changing walls, portable electronics and fashion accessories, for instance, would not require pixelization and would add significant aesthetic value. An even closer target could use P-Ink's voltage-tunable color to actually measure voltage. Preliminary results involving connecting a P-Ink cell to a disposable battery (Fig. 7) clearly show how such a cell could be installed as an onboard sensor to display brightly the state of charge and state of health of a diversity of battery types.

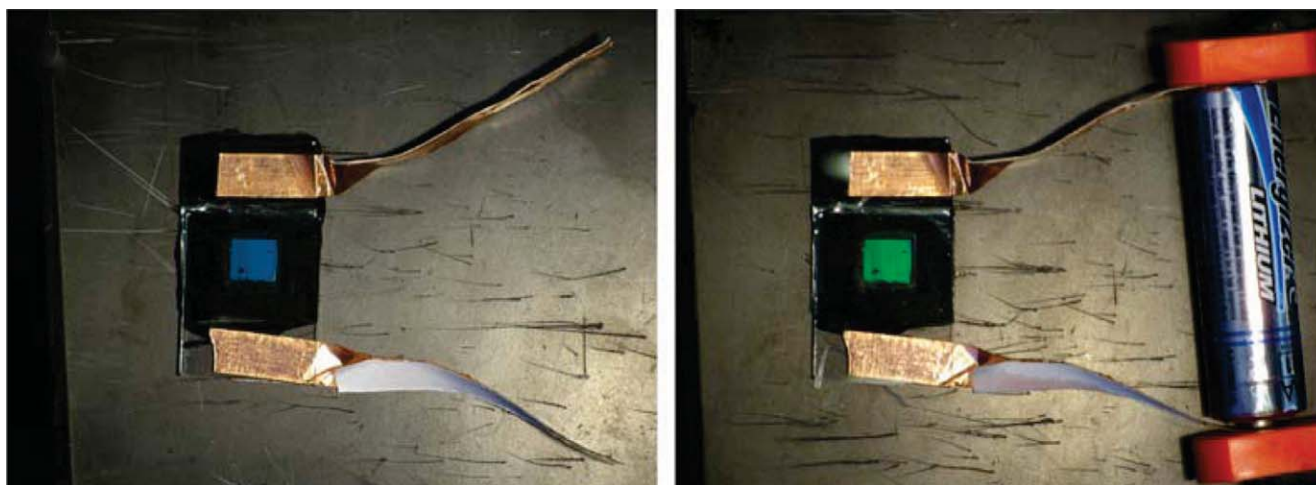


Fig. 7 A P-Ink device reflecting (A) blue, when unconnected to a power supply, and (B) green, when connected to a 1.5 V AA battery.

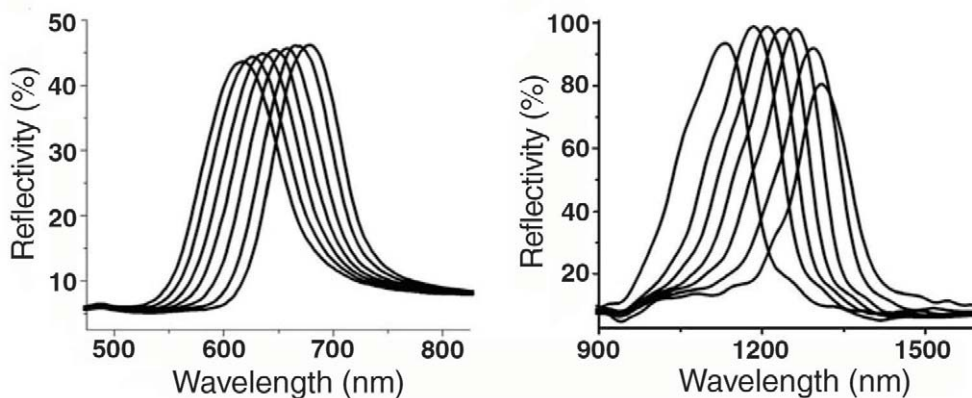


Fig. 8 Mechano-optical behavior of Elast-Ink: reversible compression–decompression cycles causing the reflected color to shift through the visible (a) and near-infrared (b) spectral wavelength ranges.

Elast-Ink

A distinct yet related technology to P-Ink, also with promising market potential, is called Elast-Ink, a soft and elastic inverse opal responsive to mechanical pressure. This material can easily be compressed, changing the layer spacing between the air voids, thereby causing its color to gradually shift across the entire visible spectrum as increasing pressure is applied (Fig. 8). Using this mechano-optical effect, a highly sensitive, color-tunable device has been demonstrated, wherein Elast-Ink replicates in full color and with high fidelity the fingerprint of an individual (Fig. 9). Given that Elast-Ink is sensitive to mechanical pressure, the target markets for this technology are completely different from those for P-Ink, which focuses on full-color coatings of different kinds. The most attractive feature of the Elast-Ink technology is its high sensitivity to pressure, and the striking color changes that result. This makes it an ideal technology for an anticounterfeit security



Fig. 9 A full-color fingerprint visualized using an elastic photonic crystal, overlaid onto a grayscale image of an index finger.

device, where an unassisted human user, without the intervention of machines, could press on the material and directly observe the dramatic color changes and subsequent relaxation back to the original state once pressure is removed. Such a feature would be easy to use, and practically impossible to duplicate.

Does Elast-Ink have a future?

The need for new and more secure anticounterfeit devices has never been more acute. Currency is a particularly vulnerable market, heavily targeted by criminals ranging from casual counterfeiters all the way to state-sponsored operations, with worldwide yearly printing of about 200 bn notes. An equally vulnerable market is the global trade in pharmaceuticals, with an estimated market size of \$600bn for 2005. Although it is difficult to obtain exact figures, it is estimated that 10% of all drugs on the global market are counterfeit, and in certain countries this figure may be as high as 50%. In addition to the significant economic losses, around US\$30–40bn, this problem has dire consequences on human health. It is therefore imperative that new security measures be developed so that the public can ensure their life-saving and life-extending medications are legitimate. Elast-Ink could help hundreds of millions of people around the world by ‘extending’ itself into this market.

As with the P-Ink technology, we have had to surmount several technical challenges during the development of Elast-Ink. These ranged from the demonstration of a mechanically actuated elastic inverse opal sensitive enough to detect human finger pressure, to the optimization of the system to achieve quantifiable and reproducible metrics through to the development of a process that could be translated to large-scale fabrication. This is work in progress and, not surprisingly, there is still a significant amount of research that must be done before any products will reach the market. One of the first tasks is to demonstrate large-scale manufacture through a pilot production plant. A full battery of stability tests will also be essential, with these tests varying greatly depending on the application. Features on the packaging of luxury goods obviously do not need the durability of features on banknotes,

which circulate widely, are subjected to torturous handling such as crumpling and inadvertent passage through washing machines, plus they need to last for at least 1–2 years. Another crucial part of the research ahead will be to make distinct variants of our technology so that it can be sold to different markets without compromising on the security of any customer's product.

In addition to security-related items, we see Elast-Ink as a broad-based platform for technologies such as piezoelectric-driven color displays, accelerometers for automobile airbag release, sensors to monitor shockwaves from explosions, detectors for earthquake-created vibrations and strain in high-rise buildings, and monitors for fluid and gas pressure.

Closing thoughts

Having written a materials chemistry lab-to-market paper for the first time, the authors can only agree wholeheartedly with Philip Ball, an editor of *Nature* who once remarked 'a scientific breakthrough is a discovery pregnant with promise and then the hard graft begins'. Most scientists would agree with this statement and this has certainly been our experience, starting in the days of innocent academia when we worked on purely curiosity-driven scientific ideas at the leading edge of our field inspired by the natural excitement, satisfaction and beauty of creating new knowledge for the good of humanity.


In the academic era before today's industrialization of the university, it was normal in the so-called old model of wealth creation for industry to recognize the technological relevance of freely published ideas in the open literature emerging from university science laboratories, to create a portfolio of intellectual property based on these ideas considered commercially relevant, and to invest in research and development geared towards transforming these ideas into real products. This strategy for technology transfer from university to industry worked pretty well; it created wealth for the company, employees and the nation, and occasionally the academics who actually dreamed up the ideas in the first place made some money!

We believe the jury is still out on whether the old academic model of wealth creation is better or worse than the new post-academic model, a good example of which has been outlined here. The concept behind the post-academic model is that the wealth of

a nation is intimately connected to the control and development of its intellectual property, and in a highly competitive world of global science, technology and trade it is perhaps best if the university and its academics participated more actively in the technological development of their scientific ideas by the creation of new companies.

In our opinion, university academics and their technology transfer organizations, as well as industry researchers and their managers, are still grappling with how to best handle and benefit from these changes. This is a challenge to all concerned. From our perspective, academics who are inspired to found a start-up such as Opalux have to decide what level of involvement in the company is best for their personal circumstances. Whether to throw in their academic career and become chief executive or technical officer in the company or remain an academic or maybe opt for an intermediate role such as senior scientific advisor is usually a life-changing decision.

By choosing the company route, an academic has to come to terms with the extremely complex and heavy demands of patent strategy and technology transfer, business and capital investment, finance and law, to name but a few of the survival crash courses that cannot be side-stepped. And equally challenging is risk management: one must learn to live and sleep with a certain amount of unavoidable personal liability. But all of this can be compensated for by the tremendous satisfaction of starting a new company to develop and commercialize one's ideas, ultimately to create economic benefits for the founders and employees, university and investors, taxpayers and the nation.

This is a brief synopsis of what the authors perceive as the trials and tribulations of the post-academic world and accounts for some of the personal challenges they have had to confront on a daily basis with the founding and management of Opalux, which they believe has a bright and truly colorful future. 

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