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Plasmonic Color Makes a Comeback

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Rachel Brazil

The phenomenon behind the earliest photographs is inspiring new research in color printing and displays.

One of the earliest surviving photographs shows the mortuary temple of Pharaoh Ramses II, located in the ancient Egyptian capital of Thebes. The sharp clarity of the image, showing a building with a golden glow framed by a blue sky, gives the impression that it could be a modern snapshot, but the image, now in the Metropolitan Museum of Art, was taken in 1844.

Rather than being captured by modern, high-resolution methods, this early photograph, called a daguerreotype, was made by exposing a silver iodide-coated surface to light, creating clusters of elemental silver 1−2 nm in diameter. The image was developed with mercury vapor, forming silver−mercury nanoparticles, which scatter light and create the final scene, embodying a resolution impressive even by today's standards. Two centuries later, the technology responsible for this earliest of photographs is making a comeback: it is inspiring the next generation of ultra-high-resolution color printing and displays.

Shining light on metallic nanoparticles causes free electrons on their surfaces to oscillate, leading particular wavelengths to be absorbed and others to be scattered, resulting in what's known as plasmonic color. The specific color produced depends on particle size and shape and the relative positions of particles. Although Louis Daguerre did not understand the phenomenon behind the photographic method he presented in Paris in 1839, plasmonic color was the basis of the daguerreotype.

Daguerreotypes were essentially black and white images, with light and dark tones created according to the density of

Created in 1844, this daguerreotype of Pharaoh Ramses II's mortuary temple in Thebes has the sharp clarity of a modern photograph. Credit: Metropolitan Museum of Art.

the silver-mercury particles. But they also have the curious property of producing hints of color, which change with viewing angle because of the plasmonic properties of the particles. The producers of these early photographs realized they could take advantage of these effects to deliberately introduce color to their images. For example, they developed an overexposure process known as solarization to create vivid blue skies. A recent investigation by the Metropolitan Museum of Art attributed this color to a larger number of silver nucleation sites, which ultimately led to smaller nanoparticles, creating a bluer tone.

Scientists now are returning to these color-tuning effects to create full-color images—both static and dynamic. Plasmonic color offers advantages over the chemical dyes and pigments that are usually used to produce color: it requires only small numbers of metallic nanoparticles to create ultra-high

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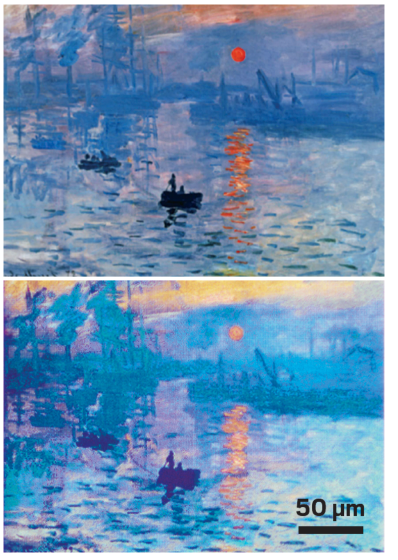
resolution with high durability, and at low cost. One major difference from most existing display technologies is that plasmonic-color displays use reflected light rather than requiring backlighting from light-emitting diodes (LEDs), used today in televisions. As well as being easier to view in sunlight, this also means they use much less power.

Although prototype devices using plasmonic color are starting to appear, to become commercially viable they will need to compete with established technologies. Current liquid-crystal display (LCD) and organic LED screens are efficient and affordable. And up-and-coming quantum dot LED displays that are supported by major technology players such as Samsung and Apple can make use of many already well-established industrial production processes. Introducing a completely new technology would need significant commercial investment, which might only be viable if the right market could be identified. Until then, plasmonic color might first find its niche in specialty applications such as anticounterfeiting and even virtual reality.



A microscale reproduction (bottom) of Claude Monet's "Impression, Sunrise," (top) uses plasmonic color generated by patterns of aluminum nanostructures. Credit: *Nano Lett.* **2014**, DOI: 10.1021/nl501460x. Original image adapted by the researchers with permission from Musée Marmottan Monet in Paris, France/Giraudon/Bridgeman Images.

Printing and painting with plasmonics

Color photographs are printed with organic inks, which can fade over time. But an image printed with plasmonic color would be a fade-proof combination of stable gold, silver, or aluminum nanoparticles of different sizes. Plasmonic nanoparticles are better than anything else in nature at scattering light, explains Jake Fontana, a plasmonics researcher at the Naval Research Laboratory. That means that plasmonic color images only need a fraction of the material that color photographs do to produce color.

Plasmonic color is a subset of structural color, which is color resulting when the micro- or nanostructure of a material causes light scattering and interference. One form of structural color is the iridescent blue of the *Morpho* butterfly's wings, whose scales have branched nanostructures that scatter light in complex ways. In plasmonic color, the color arises from light absorption and scattering off of the nanoparticles themselves. As with other forms of structural color, size, shape, and patterning create the color rather than chemical composition.

Debashis Chanda, a nanophotonics scientist at the University of Central Florida, recently developed a plasmonic paint. Using plasmonic effects, Chanda created a color spectrum of highly reflective metallic pigments made from flakes of a plasmonic material that he says can be formulated into paint, cosmetics, printer ink, and color displays. Because the pigments can also be formulated to reflect infrared light and several types of radiation, including X-rays, Chanda's plasmonic coatings can also work as coolants or radiation shields.

One of the initial problems with plasmonic color, as seen in daguerrotypes, is its viewing angle dependence—a significant drawback for a television screen or billboard. The effect is caused by the arrays of particles diffracting light, splitting it into different wavelengths at varying outgoing angles. According to Joel K. W. Yang, a nanoscientist at Singapore University of Technology and Design, one way around this is to space the nanostructures no more than 250 nm apart, which is roughly less than half the wavelength of visible light and will prevent diffraction from occurring.

Yang has developed an approach for plasmonic color printing that involves using electron beam lithography to pattern aluminum disks of different diameters on top of 250 nm tall nanopillars on a surface. Each disk-topped pillar acts as an individual color pixel. "Simply by changing the diameter of the disks, we can change the color," Yang says. So far, he has printed on silicon, glass, and even thin polymeric films.

His images have a resolution of 100,000 dots per inch (39,370 dots per cm), which is at least 1,000 times as high as that of an inkjet printer and reaches the fundamental diffraction limit, which is the maximum resolution that can be achieved by any optical system.

The fabrication method is expensive and slow, but Yang is looking at developing the method for anticounterfeiting applications, in which applying patterns at such high resolution could hamper easy replication. Although he can make a palette of more than 300 colors, it does not yet cover the

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entire gamut of colors visible to the human eye. Yang admits that some colors are more difficult to create than others: "We haven't yet achieved pure red but have some ideas on how to get around it."

Reflective displays

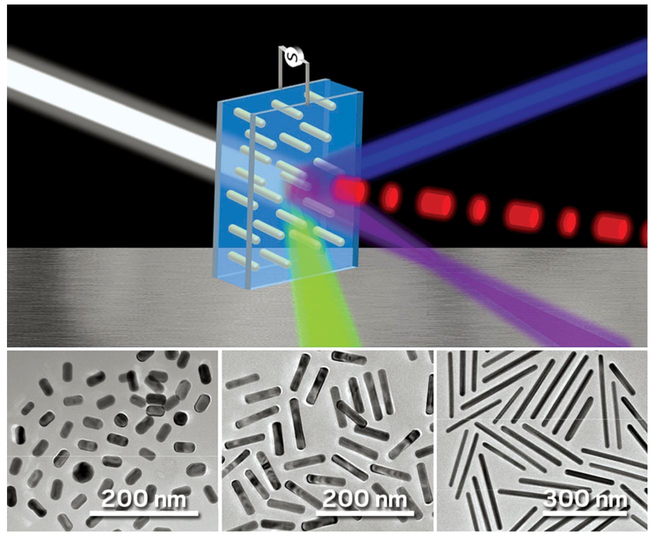
Plasmonic color has the potential to pack more pixels into less space, which makes it attractive for dynamic display technology. What's more, because plasmonic displays wouldn't need backlighting, "you could save a lot of power," says nanochemist Andreas Dahlin of Chalmers University of Technology. "For us, that's the main driving force" in working to develop dynamic plasmonic displays, he says.

Many labs are still working out how to develop plasmonic color most effectively into new display technologies, but Chanda has already produced a prototype flexible plasmonic display and launched a start-up company, E-skin Displays, in 2017. He combined existing LCD technology with plasmonic color by patterning shallow nanosized wells in aluminum using nanoimprint lithography and then covering them with a liquid-crystal layer. The wells, like nanoparticles, support plasmonic resonances. Applying a voltage across the device reorients the liquid crystals, which alters the plasmonic response and the color. These types of displays could one day be used for large-scale, low-energy-consumption, dynamic billboards.

Another problem for plasmonic color systems is creating a black hue because it requires a combination of subpixels that would absorb light consistently across the whole visible spectrum. But Chanda says E-skin Displays now has a solution that integrates black and gray, work that is not yet published.

The Naval Research Laboratory's Fontana has a different approach to making dynamic plasmonic displays: using self-assembled colloidal gold nanorods suspended in toluene. By placing an electric field across the suspension, the nanorods align in the direction of the applied field, producing intense plasmonic color, Fontana explains. The system is fast; it can switch at least 1,000 times as quickly as a conventional liquid-crystal pixel, potentially cutting down on motion blur, which is a problem with LCD displays.

In current commercial displays, each pixel is actually made of a red, green, and blue subpixel. Different amounts of light from each subpixel mix to create the perception of any color desired. One ambition for those developing plasmonic color systems is to flip one pixel between red, green, and blue rather than needing three separate subpixels—that would require less space, allowing for much smaller pixels and higher definition screens. A system that can do just that has been created in the lab of Jeremy Baumberg at the University of Cambridge. It uses gold nanoparticles coated in the conducting polymer polyaniline and sprayed onto a flexible mirrored surface. The mirrored surface amplifies the plasmonic resonance, resulting in a more intense, uniform color with no viewing-angle dependence.



A plasmonic color pixel consists of a suspension of gold nanorods in toluene (top). Applying a voltage aligns the nanorods and changes the color of light transmitted when white light hits the pixel. Using nanorods of different sizes and shapes (bottom) in the pixel yields different colors. Credit: *ACS Nano* **2019**, DOI: 10.1021/acsnano.9b00905.

The color of each pixel is tuned by the reversible oxidation and reduction of the polymer, which changes the polymer's refractive index and shifts the system's plasmonic resonance. Each nanoparticle can theoretically be tuned independently, providing a potential spatial resolution of less than 100 nm. So far, the researchers have created pixels that switch only between red and green, but they are working on blue. Silver or aluminum particles could potentially show blue color, but "there is always a trade-off, as silver and aluminum materials are chemically [more] unstable [than gold]," says Hyeon-Ho Jeong, who formerly worked as a postdoc with Baumberg at Cambridge and is now at Gwangju Institute of Science and Technology.

Plasmonic color's prospects

It's not yet clear whether plasmonic color can beat existing screen technologies in the mass consumer market. Current LED technology can already provide ultra-high-definition images, with even higher-resolution, 8K (7680 x 4320 pixel) screens around the corner. "I don't think we can ever produce something that gives you a better image quality than LED displays, but we can produce something that gives you a good image quality, and it will cost you a lot less," Chalmers University's Dahlin says. Chanda says large technology companies are watching developments in

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plasmonic color carefully but seem reluctant to jump in just yet. He adds, however, that “we are ready when there is a big partner on the horizon.”

The problem is finding the “killer app,” according to Bahman Taheri, CEO of AlphaMicron, a company focused on liquid-crystal photonics and based in Kent, Ohio. “LCDs had been around for a while and didn’t overtake cathode ray tubes for 10 years,” he says. “It only really started to take over when it had a killer app, and that was the laptop.” Taheri suggests a niche application such as virtual reality headsets could be the way to open the door. They need a large field of view for the user, and “the pixel size and the level of detail become really critical,” he says.

“I think we are just at the beginning of this new dynamic plasmonics [field],” Fontana says. Taheri agrees, saying the technology is still “a diamond in the rough.”

Rachel Brazil is a freelance contributor to Chemical & Engineering News, the weekly newsmagazine of the American Chemical Society.

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