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Researchers want to mimic structural colors found in Nature to make sensors, displays, and even art.

science lab is an odd place of work for an artist. But more than a decade ago, a brush with butterfly wings sent Kate Nichols down an unlikely career path, leading to her current position as artist-in-residence in a chemistry lab.

The wings that triggered everything were those of a Morpho butterfly. In a college science class, Nichols first learned that the wings' iridescent blue color does not come from a pigment, but instead from layered sheets of chitin, a colorless sugar polymer. The microscopic arrangement of the sheets reflects certain wavelengths of light and blocks others, producing a pure, shimmering blue.

Morpho butterflies are not the only animals that generate color through this pigment-free phenomenon, known as structural color. Blue bird wings derive their color from varying patterns of melanin granules, the color-shifting skins of octopuses rely on guanine nanocrystals, and the blue patches of mandrill monkeys' faces come from ordered, parallel strands of collagen fibers. In fact, microbes, plants, and just about every animal family include species that use structural color. These biomolecular structures interfere with, reflect, or transmit specific wavelengths of light—creating hues from colorless materials. This play of light through nanoscale structures tints the natural world.

Having learned about structural color in college, Nichols wanted to find a way to use the phenomenon to produce vibrant colors in art. Now, in Paul Alivisatos's lab at the University of California, Berkeley, she works alongside chemists to produce a palette of silver nanoparticles for her paintings.

Nichols is not alone in her interest in this colorful molecular phenomenon. In the last several years, new technologies have improved the ability to visualize and engineer nanoscale structures—allowing researchers to study and create structural colors. Scientists have been cataloging and teasing apart how species across the animal kingdom create these colors.



Most blues in Nature, such as those seen in this Morpho butterfly (*Morpho menelaus*), are the result of structural color. Credit: Derkarts/Wikipedia.

This has inspired materials scientists to take that knowledge and re-engineer Nature's tricks to produce synthetic forms of structural color. "Harnessing or understanding how natural structural colors work will allow us to make materials in in the lab that we previously couldn't—to guide light or sense it, and create coatings and other materials", says Richard Prum of Yale University.

We now know structural color appeared on the scene long ago. Scientists have found multilayered nanostructures in the cuticles of 550-million-year-old beetle fossils that still displayed structural color. Surrounding biological materials deteriorated over time, shifting the colors toward longer wavelengths, but scientists could estimate the insects' original colors from the nanoscale patterns. It is uncertain whether the insects evolved the structures for the color itself, or if the structures had some other function and the color was just an artifact—like the iridescent mother of pearl lining of mollusk shells. Those colors probably evolved as a byproduct of the molecular arrangement that gives the shells their strength, says Matthew Shawkey of the University of Akron.

Still, new research, some by Shawkey's group, shows that once structural color evolved, it became easy to tweak. Closely related species can produce different colors using variations on the same mechanism. For example, Shawkey studied purple, blue, and green patches on the wings of 29 duck species and

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Etching holes of different-sized diameters through a three-layer sheet of silver and silica produces different shades of color (insets). Credit: Adapted from X. Yang et al., *Scientific Reports*.

found that the colors depended on the size of melanin particles, the spacing between those particles, and the arrangement of particle layers in the feathers.

Despite the simplicity with which Nature can vary color, certain hues dominate the structural color palette. Nearly all blues, whether in butterflies, birds, or beetles, are of structural origin. Reds, on the other hand, are almost always formed by pigments.

Other studies demonstrate that Nature has experimented with a range of structures to produce color. For example, Prum recently studied structural colors from 127 arthropod species using X-ray scattering and electron microscopy. They identified a rich range of nanostructures, including packed spheres, columns, perforated sheets, and sponge-like shapes made from chitin and other materials. The researchers think that these structures are formed by using contorted cell membranes as templates. The range of structures observed implies that "evolutionarily, insects and arthropods have exhaustively explored the physical possibilities of how to make a nanostructure by bending and folding a membrane", Prum says.

With a growing catalog of examples of how Nature produces structural colors, researchers are now trying their hand at making them. Synthetic materials with structural color would have two major advantages over pigments. Pigment compounds produce color by absorbing a range of visible wavelengths of light. Over time, the sun's light can break down the compounds, which causes the colors to fade. Structural color, instead, produces hues when light physically interacts with nano- and microscopic structures, meaning they are more resistant than pigments to fading. Also, because the spacing between these structures is on the same general order as the wavelengths of light that the materials trap, reflect, or transmit, they can produce purer colors than pigments can.

Some scientists have formed structural color by adjusting the spacing between packed nanoparticles. Other groups have done it by printing holes or creating cracks in sheets of materials. And some researchers have synthesized colloidal fluids that can be hydrated and dehydrated to change colors. Different strategies will work for different applications, says Vinothan Manoharan, a physicist at Harvard University. For example, he says, materials that work well as paints may not be the best to create color for electronic displays.

To create brightly colored images that could be used as security markings on credit cards, Xiaodong Yang, an engineer at Missouri University of Science and Technology, and his colleagues etched holes into films of silica sandwiched between two thin layers of silver. By changing the diameter, spacing, and depths of the holes, the team could change the wavelengths of light absorbed or reflected.

Structural colors also could serve as sensors. These materials would change their structures, and thus their color, in response to the presence of certain chemicals. In the Alivisatos lab, for example, graduate student David Litt works with gold nanoparticles stitched together by pieces of DNA. When toxins or DNA-cutting enzymes reconfigure or break down the DNA, the spacing between the particles changes, producing a detectable shift in color.

Shu Yang, a materials scientist at the University of Pennsylvania, has developed structural color sensors that detect extreme physical forces such as those from a bomb blast or the collision between football players. The sensors consist of a diamond-like crystal lattice of a polymer. When hit by a shockwave, pores between polymer particles widen, and nanoscale layers fracture. As a result, the material shifts its color from red-orange to green, blue, or purple, depending on the strength of the force. Yang envisions using the materials as sensors on the helmets of football players or military personnel to help alert doctors to possible traumatic brain injuries. In a study in rats, the sensor's color change corresponded to the degree of brain injury in the animals when hit with a blast of compressed air that simulates an explosion.

To create structural colors for use in displays and paints, Manoharan and others have turned to colloidal materials. Unlike many structural colors, these materials are not iridescent and look the same from all angles. As in Nature, producing matte blues was easy. But creating a colloidal red was difficult. Manoharan's group finally did so by "essentially making a particle that is both large and small at the same time." These particles have a small light-scattering core made of polystyrene and an outer shell made from a different polymer that swells and shrinks when hydrated and dehydrated, respectively. The shell size sets the interparticle distances, allowing the researchers to cycle through a rainbow of pure colors as they dry or add water to the colloidal suspensions. "It's important to keep in mind that the development of structural colors in Nature is based on a different set of constraints than we would have for applications in the lab or in industry", Manoharan says. "The fact that birds don't make red structural colors doesn't mean it's impossible for us to do so."

A benefit of the hydration strategy for structural color is that researchers can use one material and, with a simple physical change, produce a range of colors. This is ideal for making commercial paints and coatings that need to be manufactured consistently, maintaining the same exact color across batches. To use such a system in displays, Manoharan will need to find



Artist Kate Nichols created this piece by layering millions of silver nanoparticles between sheets of glass. Credit: Art by Kate Nichols, photo by Donald Felton.

a way to switch between colors quickly, such as in response to a changing electric field. That may be difficult, he says.

Back in the Alivisatos lab, Nichols is not bound by the need to produce exactly the same shades each time. She has created iridescent blues, ambers, reds, and mossy greens from silver salts that she coaxes to crystallize into patterned nanostructures. Nichols picks her structures simply for shimmering colors that grab the viewer's eye—just as the blue wings of Morpho butterflies caught her attention years ago.

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