Chemical reaction alters the colours of plasmonic prints

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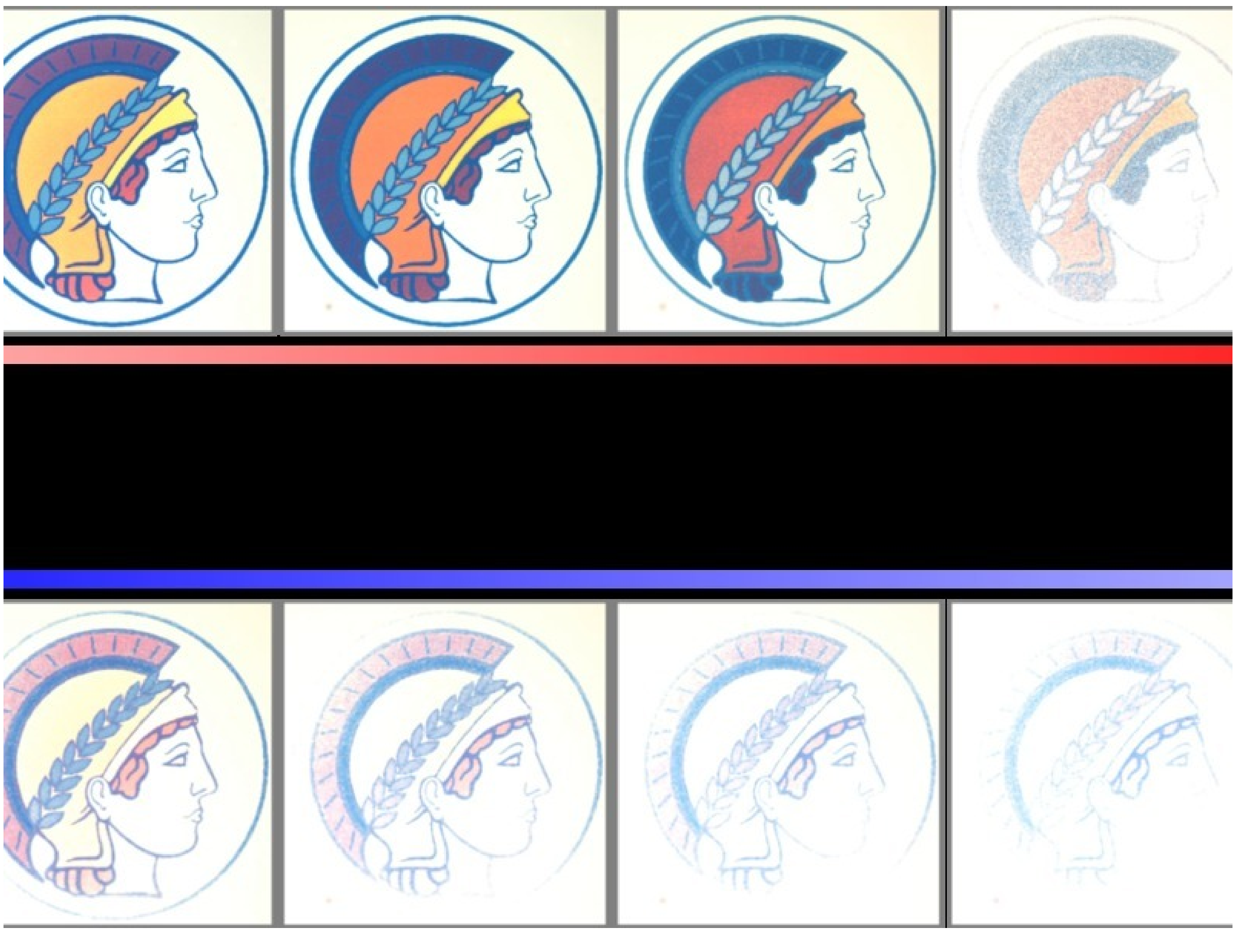

Colour changes. Credit: Nature Communications 2017 / MPI for Intelligent Systems

Plasmonic printing produces resolutions several times greater than conventional printing methods. In plasmonic printing, colours are formed on the surfaces of tiny metallic particles when light excites their electrons to oscillate. Researchers at the Max Planck Institute for Intelligent Systems in Stuttgart have now shown how the colours of such metallic particles can be altered with hydrogen. The technique could open the way for animating ultra-high-resolution images and for developing extremely sharp displays. At the same time, it provides new approaches for encrypting information and detecting counterfeits.

Glass artisans in medieval times exploited the effect long before it was even known. They coloured the magnificent windows of gothic cathedrals with nanoparticles of gold, which glowed red in the light. It was not until the middle of the 20th century that the underlying physical phenomenon was given a name: plasmons. These collective oscillations of free electrons are stimulated by the absorption of incident electromagnetic radiation. The smaller the metallic particles, the shorter the wavelength of the absorbed radiation. In some cases, the resonance frequency, i.e., the absorption maximum, falls within the visible light spectrum. The unabsorbed part of the spectrum is then scattered or reflected, creating an impression of colour. The metallic particles, which usually appear silvery, copper-coloured or golden, then take on entirely new colours.

A resolution of 100,000 dots per inch

Researchers are also taking advantage of the effect to develop plasmonic printing, in which tailor-made square metal particles are arranged in specific patterns on a substrate. The edge length of the particles is in the order of less than 100 nanometres (100 billionths of a metre). This allows a resolution of 100,000 dots per inch – several times greater than what today's printers and displays can achieve.

For metallic particles measuring several 100 nanometres across, the resonance frequency of the plasmons lies within the visible light spectrum. When white light falls on such particles, they appear in a specific colour, for example red or blue. The colour of the metal in question is determined by the size of the particles and their distance from each other. These adjustment parameters therefore serve the same purpose in plasmonic printing as the palette of colours in painting.

The trick with the chemical reaction

The Smart Nanoplasmonics Research Group at the Max Planck Institute for Intelligent Systems in Stuttgart also makes use of this colour variability. They are currently working on making dynamic plasmonic printing. They have now presented an approach that allows them to alter the colours of the pixels predictably – even after an image has been printed. "The trick is to use magnesium. It can undergo a reversible chemical reaction in which the metallic character of the element is lost," explains Laura Na Liu, who leads the Stuttgart research group. "Magnesium can absorb up to 7.6% of hydrogen by weight to form magnesium hydride, or MgH2", Liu continues. The researchers coat the magnesium with palladium, which acts as a catalyst in the reaction.

During the continuous transition of metallic magnesium into non-metallic MgH2, the colour of some of the pixels changes several times. The colour change and the speed of the rate at which it proceeds follow a clear pattern. This is determined both by the size of and the distance between the individual magnesium particles as well as by the amount of hydrogen present.

In the case of total hydrogen saturation, the colour disappears completely, and the pixels reflect all the white light that falls on them. This is because the magnesium is no longer present in metallic form but only as MgH2. Hence, there are also no free metal electrons that can be made to oscillate.

Minerva's vanishing act

The scientists demonstrated the effect of such dynamic colour behaviour on a plasmonic print of Minerva, the Roman goddess of wisdom, which also bore the logo of the Max Planck Society. They chose the size of their magnesium particles so that Minerva's hair first appeared reddish, the head covering yellow, the feather crest red and the laurel wreath and outline of her face blue. They then washed the micro-print with hydrogen. A time-lapse film shows how the individual colours change. Yellow turns red, red turns blue, and blue turns white. After a few minutes all the colours disappear, revealing a white surface instead of Minerva.

The scientists also showed that this process is reversible by replacing the hydrogen stream with a stream of oxygen. The oxygen reacts with the hydrogen in the magnesium hydride to form water, so that the magnesium particles become metallic again. The pixels then change back in reverse order, and in the end Minerva appears in her original colours.

In a similar manner the researchers first made the micro image of a famous Van Gogh painting disappear and then reappear. They also produced complex animations that give the impression of fireworks.

The principle of a new encryption technique

Laura Na Liu can imagine using this principle in a new encryption technology. To demonstrate this, the group formed various letters with magnesium pixels. The addition of hydrogen then caused some letters to disappear over time, like the image of Minerva. "As for the rest of the letters, a thin oxide layer formed on the magnesium particles after exposing the sample in air for a short time before palladium deposition," Liu explains. This layer is impermeable to hydrogen. The magnesium lying under the oxide layer therefore remains metallic – and visible – because light is able to excite the plasmons in the magnesium.

In this way it is possible to conceal a message, for example by mixing real and nonsensical information. Only the intended recipient is able to make the nonsensical information disappear and filter out the real message. For example, after decoding the message "Hartford" with hydrogen, only the words "art or" would remain visible. To make it more difficult to crack such encrypted messages, the group is currently working on a process that would require a precisely adjusted hydrogen concentration for deciphering.

Liu believes that the technology could also be used some day in the fight against counterfeiting. "For example, plasmonic security features could be printed on banknotes or pharmaceutical packs, which could later be checked or read only under specific conditions unknown to counterfeiters."

It doesn't necessarily have to be hydrogen

Laura Na Liu knows that the use of hydrogen makes some applications difficult and impractical for everyday use such as in mobile displays. "We see our work as a starting shot for a new principle: the use of chemical reactions for dynamic printing," the Stuttgart physicist says. It is certainly conceivable that the research will soon lead to the discovery of chemical reactions for colour changes other than the phase transition between magnesium and magnesium dihydride, for example, reactions that require no gaseous reactants.

More information: Xiaoyang Duan et al. Dynamic plasmonic colour display, *Nature Communications* (2017). DOI: 10.1038/NCOMMS14606