Bright new world

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A strange discovery could spark a nanotechnology revolution, bringing perfect lenses, rapid medical tests and superfast computers. Bruce Schechter welcomes the dawn of plasmonics

THOMAS EBBESEN holds a piece of gold foil up to the light and looks through it. Made 14 years ago by technicians at the NEC Research Institute in Princeton, New Jersey - where Ebbesen was working at the time - at first glance the foil looks unremarkable. Peer at it under an electron microscope, though, and you would see that it is peppered with 100 million identical holes, each 200 times narrower than a human hair. But there's something much more extraordinary about the thin gold film: more light passes through the holes than strikes them.

It is a finding that challenges our entire understanding of light. According to optical theory, at 300 nanometres across the holes are so small they should only let through 0.01 per cent of the visible light that falls directly on them. But Ebbesen's experiment suggested they were transmitting more than 100 per cent. Somehow the metal was acting like a funnel, channelling all the light that hit the film through the nanoscale pores.

The phenomenon not only has theorists rethinking their approach to optics. It has sparked a new research effort called plasmonics that is revolutionising what we can do with light. Soon we could be using the surface of metals to shuttle information at the speed of light around electronic circuits no bigger than a few atoms wide. And it may not be too long before diabetics are thanking plasmonics for their daily dose of insulin. "Plasmonics is going to be the next big thing in nanoscience," says Naomi Halas, who works as a chemist at Rice University in Houston, Texas.

Until recently, to question the theory of light would be unthinkable. For over a century, scientists have believed that it is impossible to see features smaller than the wavelength of the light illuminating them. According to classical optics, that's because light scatters from every point on an object, sending out waves like ripples on a pond.

Drop two stones into water and you see the waves overlap with each other. If the stones are far apart, the pattern of ripples from each stone shows up clearly and you can tell that two stones were thrown into the water. But if the stones are close together when they plunge into water, the interference pattern is so blurred you can't tell how many stones were tossed in.

The same thing happens to light waves bouncing off an object. In fact the only light waves that can travel any distance - the ones that we see when we look at an object - come from points separated by about the wavelength of light. This is known as the diffraction limit and it appears in every textbook on optics.

By the same reasoning, light hitting a screen filled with holes smaller than its wavelength interferes strongly. In fact the interference is so strong that barely any light appears to make it from one side to the other. Instead most of the light's energy is trapped close to the screen in the form of an evanescent or surface wave. So Ebbesen was astonished to see sunlight streaming through holes just 300 nanometres across, much shorter than the wavelength of visible light.

At first he thought something was wrong with the gold foil, which was originally made for an experiment to test the quantum theory of electromagnetic interactions. But a quick look at its surface under an electron microscope showed that it was perfect. He got an even bigger surprise when he found the holes were transmitting far more light than was falling directly on them. "That really baffled me," recalls Ebbesen who is now at the Louis Pasteur University in Strasbourg.

Ebbesen had more samples made and confirmed his results. But no one could explain his bizarre findings. Amazingly, he did not publish his work. And without any theoretical understanding of the phenomenon, NEC didn't bother to patent the discovery. Ebbesen put the puzzle aside.

The experiments remained a mystery until 1998 when theorist Peter Wolf joined NEC and heard about Ebbesen's strange results. Wolf specialises in calculating how electrons behave in metals. On the surface of a metal, electrons can wander around freely to form a two-dimensional ocean that can ripple with waves called surface plasmons. Wolf realised that light striking a metal surface could set the electron sea vibrating. And he worked out that if the frequency of the light hitting the metal somehow matched the resonant frequency of the surface plasmons, it could cause the bizarre effects that Ebbesen was seeing. Wolf suggested some more experiments to confirm his theory, and in 1998 they finally published news of the phenomenon in *Nature* (vol 391, p 667), nine years after the original discovery.

Wolf and Ebbesen had showed that light makes it through the holes by being converted briefly to surface plasmons in the metal and then back again. But this only happens when the light and surface plasmons have the same energy and momentum. This is not the case for a smooth, shiny metal but the situation is different for metals with holes punched in them. The holes adjust the energy of momentum of the surface plasmons just enough so they match the light. Get the size of the holes right and when light of a particular wavelength strikes the metal, the surface plasmons begin to resonate. On Ebbesen's foil, the surface plasmons accumulate the electromagnetic energy of the light and concentrate it around the holes.

Because surface plasmons compress electromagnetic energy into this tiny volume, they create an intense electric field that holds the key to their many applications. In Ebbesen's foil the intense field around the hole is able to penetrate through to the other side of the metal, where it excites a second set of surface plasmons. These convert the energy back into light. So while light appears to flood through the foil, it isn't the same light that hit the metal in the first place.

Scientists have known about surface plasmons since the 1950s, but it is only recently that they have been able to sculpt nanoscale structures in metals. To punch millions of holes in a piece of gold foil the size of a postage stamp, NEC's technicians used gallium ions that can be focused with electric fields into a beam just a few nanometres wide. But textured surfaces are not the only way to harness surface plasmons - many researchers prefer to form surface plasmons on metal nanoparticles they have cooked up in the lab.

So far, the most far-reaching potential application of plasmonics would be to guide photons through nanoscale circuits: a technology known as photonics. Every time you phone abroad, send an email or download a movie trailer from the Internet, you rely on light carrying vast swathes of data through fibre-optic threads. Eventually the light has to be married to electronic circuitry on its way to becoming the visual and audible information on which we rely. The marriage is an uncomfortable one because of the vast difference between the scales at which light and electronics operate. Optical fibres typically carry light with a wavelength of 650 nanometres, five times the width of the tracks on the transistors in Intel's latest Pentium processor.

To reconcile these two disparate scales, the light has to be channelled from the optical fibre into photodiodes, which convert it into electrical signals. These signals then have to be amplified before they pass into the transistors. All these extra devices ultimately prevent chipmakers shrinking circuits down to the nanoscale. It would be far better if we could do away with them completely and steer the light directly to the electronics.

Harry Atwater's team at the California Institute of Technology in Pasadena is building "waveguides" to channel light directly into a transistor on a chip. Like almost everything else in optics, the width of a waveguide can be no smaller than the wavelength of light because of the diffraction limit. To get around this constraint Atwater's team has constructed a waveguide that consists of a string of regularly spaced metallic nanospheres that run across the surface of an insulator like a trail of breadcrumbs.

The researchers shine a tiny spot of light on the first metal particle in the chain, which starts the surface plasmons vibrating on the nanosphere. If there were no other nanoparticles around, the resonating particle would re-emit light in all directions. Instead it is easier for the nanoparticle to transfer its energy by inducing an electric field in the next one in the chain. This particle interacts with the next one and so on, in much the same way energy flows from one ball bearing to the next in Newton's cradle. So far, Atwater has made waveguides measuring just 30 nanometres across - far smaller than the wavelength of light (*Nature Materials*, vol 2, p 229). The next challenge will be to find better ways to pass light in and out of waveguides, for example, by using an exceptionally narrow beam.

Some clues could come from Ebbesen's most recent work. Last year his team showed that you don't need millions of holes to funnel light through foil. One will do. All you need is a regular pattern, such as a bullseye, inscribed on the surface of the metal around the hole. The concentric circles that Ebbesen etched into his latest metal sheet concentrate the plasmons just as the holes in his original experiment do.

When light emerged from the other side of the foil it spread out in all directions, but Ebbesen wondered what would happen if he patterned both sides of the foil (see Graphic). He predicted that light would emerge in a tight beam instead of spreading, and this is exactly what happened. In fact, the emerging beam was so narrow that at first no one believed the result. Only when Ebbesen and his colleagues came up with a plausible reason for the tight beam did *Science* decide to print their article (vol 297, p 820).

The potential uses for plasmonics are not confined to optics: Ebbesen's apertures could eventually help computer manufacturers to build faster and cheaper computers. The number of transistors that can be packed onto a microchip doubles every 18 months or so. For this trend to continue, chipmakers need to find ways to carve ever-smaller circuits. At present, features as small as 130 nanometres are etched into silicon by shining ultraviolet laser light through holes in a patterned mask. But you can't keep shrinking the holes to make smaller features, because eventually you hit the diffraction limit. At this point, little light passes through the mask and the light that does gets spread out, distorting the fine features in the microchip.

Some manufacturers are considering replacing their light sources with beams of ions or electrons, which have much smaller wavelengths than light. But replacing all the existing equipment would be expensive and eventually manufacturers would hit the diffraction limit again. If Ebbesen's idea takes off, it may be much simpler and cheaper to fit his apertures to existing equipment. That way, plenty of light would pass through the masks without spreading.

Plasmonics hasn't just caught the attention of physicists and engineers. Naomi Halas and Jennifer West at Rice University in Houston believe it could revolutionise medical diagnostics and drug delivery. They work with "nanoshells", their own plasmonic creations.

Each nanoshell consists of a silica sphere coated with a thin layer of gold. The researchers make them by putting thousands of silica spheres into a pot and adding chemicals called amines. These cling to the surface of the spheres, giving them a hair-like coating. Halas and West then mix in gold nanospheres, which attach to the other end of the amine molecules. As more gold is added, it accumulates on the tips and eventually forms a shell whose thickness can be carefully controlled. By varying the thickness of the gold coating, Halas and West can precisely tune the wavelength of light that will get surface plasmons vibrating on the inner and outer surfaces of the gold shells.

Particular molecules, such as the antigens associated with HIV, can be detected in a blood sample using a technique called an immunoassay. This involves spreading a surface with certain antibodies to which the antigens will bind when blood is added. To detect the antigens, the sample is mixed with more antibodies tagged with a fluorescent dye. These stick to the end of the antigen not bound to the antibody, so the amount of fluorescence tells you how many antigens are present. The trouble is that haemoglobin in the blood absorbs this faint fluorescent glow, making it impossible to detect the presence of antigens. Until now researchers have simply removed the haemoglobin, but the purification process can be time-consuming.

Instead, Halas and West attach the antibodies to the surface of nanoshells tuned to absorb and re-emit light at certain infrared wavelengths. This is the part of the electromagnetic spectrum where the human body is most transparent, so the antigens show up even through the haemoglobin.

When the researchers shine infrared light onto the nanoshells, they detect a strong signal thanks to the surface plasmons re-emitting light. When the nanoshells are added to blood, any antigens present latch on to the antibodies. These can bind together several nanoshells in a way that changes the resonant frequency surface plasmon vibrations. This means the nanoshells absorb light with a slightly different infrared wavelength. And the shift in wavelength reveals the presence of the antigens - even in unpurified blood. As a result Halas and West have slashed the time to complete an immunoassay to just minutes. Halas believes the technique could allow paramedics to test stroke victims for specific molecular markers on their way to hospital, an advance that could potentially save lives.

They are also hoping that nanoshells coated with a polymer containing a tiny dose of insulin could one day be used to treat diabetics. Halas's team has already shown in the lab that shining a faint infrared light onto a nanoshell excites the surface plasmons and concentrates the light's energy. Enough energy builds up to melt the polymer and release the drug.

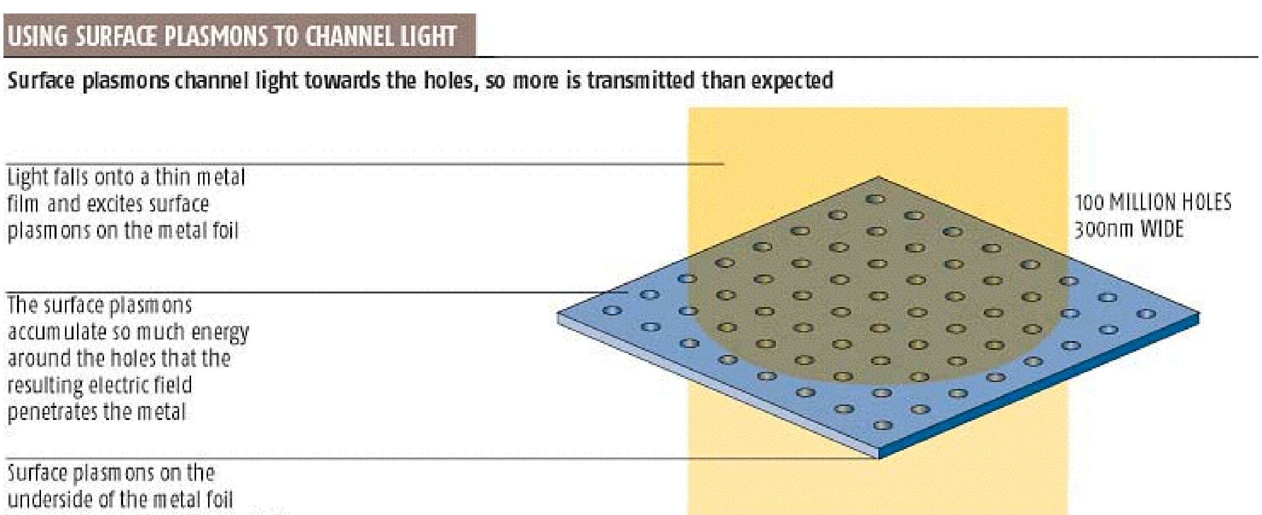
Many more tests are needed before the nanoshells reach human trials, but Halas envisions implanting small cylinders containing millions of insulin-coated nanoshells under a patient's skin. The insulin would be released simply by shining infrared light onto the skin. She thinks this could be combined with noninvasive glucose testing, which is under development in other laboratories. "It's very neat because it could all be put together into one instrument," says Halas. "Basically, people could wear a pancreas on their arm."

More speculatively, plasmonics could be used to create a "perfect lens" capable of focusing features far smaller than the wavelength of light, including single molecules (*New Scientist*, 14 April 2001, p 35). Conventional lenses are unable to resolve details smaller than a few hundred nanometres across - about the wavelength of light. Points that are closer together also produce waves that carry information about the finest details of the object, but these evanescent waves only exist near the surface. John Pendry, a theorist at Imperial College in London, believes that surface plasmons can capture the evanescent waves then amplify them to produce a perfect image - although other researchers dispute his claims.

Several groups around the world are racing to make such a perfect lens. "We're at a very early stage," says Pendry. "This is a new concept in optics, being able to do things at this very fine resolution. It's like in the very early days of optics." Think of Galileo's telescope. Now think of the Hubble Space Telescope.

Bruce Schechter is a writer based in New York

Figures:



convert the energy back into light

PLASMONIC BULLSEYE FIRES LIGHT BEAM

A pattern of concentric circles focuses light into a tight beam