ELECTRONICS AND OPTOELECTRONICS

Metal Nanoparticle Arrays
Guide and Focus Light

California Institute of Technology researchers have fabricated waveguides based on arrays of metallic nanoparticles that can strongly localize and manipulate light at dimensions below the diffraction limit, an achievement that promises optical devices smaller than the wavelength of light being propagated.

Traditionally, the minimize size of optical signaling devices has been limited by the diffraction limit (λ/2a), which is a few hundred nanometers for typical dielectric materials. Conventional waveguides are limited also in their geometry and layout by the need to avoid propagating light around sharp corners, due to the large radiative losses that occur.

Led by Harry Atwater, professor of applied physics and materials science at Caltech, the research team tested its hypothesis that the size of optical devices could be reduced below the wavelength of light being propagated by exploiting carefully engineered metal nanoparticle arrays as waveguides. The scientists also suspected that such waveguides would facilitate strong light localization, propagation around corners, and switching at dimensions below the diffraction limit.

The use of metals to form optical waveguide structures is rather counterintuitive, since metallic structures are normally opaque to light. However, Atwater’s group realized that, at the nanoscale, even metallic components become transparent.

The key to Caltech’s waveguide technology is the capability of properly arranged, uniform metal nanoparticles to transfer electromagnetic energy between neighboring particles in the array. The mechanism for this transfer is near-field interaction between adjacent nanocrystals, which sets up coupled polarization or plasmon modes.

Calculations by Atwater’s group show that 50-nm spherical particles of silver oriented with a center-to-center distance of 75 nm
New Research

Nanoparticles Added to Silver Pastes. Researchers from Sandia National Laboratories (Albuquerque, NM) added silver nanoparticles to a dispersion of micron-size silver spheres to act as a low-temperature reactive component for forming conductive particle networks. The development of conductivity depended on the arrangement of the micron-size particle network, the amount of material reacted to form necks at the contact points of the particles, and sintering of the particle network. The researchers observed that, although the nanoparticles reacted to bond the micron-size particles, the stress issues involved in nanoparticle sintering induced microscopic cracking. The Sandia team reports in the September issue of the Journal of Materials Research that critical processing variables include the state of particle dispersion, the heating rate, and the volume fraction of nanosize material.

Nanoparticles Could Inactivate Anthrax. Researchers from Clarkson University (Clarkson, NY) led by professor Richard Pacth are collaborating with scientists at the University of Florida (Gainesville, FL) on the development of nanoparticles with controlled surface properties for in vivo controlled and selective removal of overdosed drugs from the bloodstream. The cores of such particles can be metal oxides or various organic biopolymers. Control over the surface can achieve energy propagation velocities of approx. 10% of the speed of light. This is several times faster than the saturation velocity of electrons in typical semiconductor devices.

The subwavelength nanoparticle arrays, referred to by the Caltech researchers as plasmon waveguides due to the energy-guiding mechanism, can propagate light around sharp corners and through tee junctions without radiative losses. Transmission coefficients close to 100% are possible for propagation around 90 corners for certain polarizations, and the researchers calculated lossless signal splitting in tee structures.

"The biggest loss mechanism in plasmon wires is not radiation but is via internal energy loss processes that ultimately contribute to heating. Full-field electromagnetic simulations indicate that radiative losses in plasmon waveguides occur mostly at the waveguide ends," says Atwater. As a result, he believes developing designs for efficient light coupling into plasmon waveguides from bigger optical structures, such as conventional dielectric waveguides, is an important challenge.

Caltech's waveguide structures can be fabricated on dielectric substrates using electron-beam lithography, atomic force microscopy (AFM) techniques, or chemical self-assembly techniques. Each method has merit, but Atwater's group is partial to e-beam lithography at this point.

"I think that the best fabrication method for research might not be the best in some eventual application; we like e-beam lithography because we have excellent control of particle positions in arrays. Sample fabrication is however of course tedious. It's probably premature to say what's best, as is true of many things in nanotechnology," he says.

The arrays are formed from gold nanoparticles of 30 to 50 nm in size, a size range that was selected very deliberately.

"First, very small particles—sub-10 nm—exhibit broadened plasmon resonances, which is a disadvantage for our structures. Second, 30- to 50-nm particles can be obtained easily in colloidal suspensions and can be made by electron beam lithography. Third, particle sizes greater than approx. 70 nm are disadvantageous for us, since then the radiation modes of a particle include not only dipole but higher order multipole modes," says Atwater.

The current focus of the Caltech group is on exploration of the physics of these structures and assessing their technology prospects, but Atwater points out applications are some ways off.

"These structures may eventually find application in any technology that requires engineering of light localization on a deep subwavelength scale, and which can tolerate the rather high losses we expect at present," says Atwater. "One might someday foresee applications in..."
single molecule spectroscopy, improved subwavelength imaging instruments, and eventually in subwavelength scale optical wireless antennas and optical interconnects to integrated circuits or all-optical devices."

Atwater is excited about the prospects of using metal nanoparticles to facilitate light localization in devices below the diffraction limit. "But realistically there is a long way to go—at least three to five years—before any of these might become a money-maker," he says.

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Nanoantenna Structure Promises "Super Lens"

Through theoretical calculations and computer simulations, Purdue University researchers have formulated the requirements for building a nanoantenna structure that could focus optical light to a resolution smaller than its wavelength.

Key to the development is the "left-handedness" of the nanoantenna structure, which consists of carefully oriented metallic nanowires or "nanoneedles." Conventional optical materials are "right-handed"—that is, light passes through them with a positive index of refraction. Left-handed materials feature a highly unusual negative refractive index, which is expected to lead to a number of intriguing applications.

"There is the belief that it is possible with a negative refractive index material to construct a 'perfect lens' or 'super lens' that can reconstruct an image with resolution better than the incident wavelength," says Vladimir Shalaev, a professor in Purdue's School of Electrical and Computer Engineering. "With these new types of materials, it may be possible to accomplish better performance than all existing materials, in terms of making images and manipulating light."

Last year, researchers from the University of California, San Diego, fabricated for the first time a left-handed medium that could manipulate microwave radiation. "All of the work in this area so far has been done in the microwave spectral range," says Shalaev. "But nobody could suggest how one could build such a material in the optical range.

"We believe that this is the first project for how these types of materials can be used in the visible range of the electromagnetic spectrum," he says. "We did our calculations for 1.5 microns, the telecommunications wavelength."

face properties of the nanoparticles is critical so that toxins can be bound to the surfaces and deactivated. The fundamental basis for this binding is strong intermolecular interaction between electron deficient and electron enriched benzene rings. The technique might prove useful for inactivating anthrax spores that have entered the lungs.

Slow Combustion Yields Smaller Particles. A team of Argentinian researchers found that slow combustion using a nitrate-glycine gel combustion process yielded CeO$_2$-10 mol% Y$_2$O$_3$ powders with the better properties than those produced in faster reaction. The scientists paid special attention to the influence of the glycine/metal ratio and calcination temperature on powder morphology. In contrast to the usual reported behavior, the best powder characteristics (specifically, a crystallite size of 4.5 to 7.0 nm and a specific surface area of 25 to 40 m$^2$/g) resulted from slow combustion with glycine/metal ratios of 1.5 to 2.0, whereas energetic reactions produced large crystallite and particle sizes. Furthermore, they found that the crystallite size increased considerably even at moderate calcination temperatures (350 to 550°C), demonstrating the high reactivity of the nanopowders. A detailed report of this work can be found in the September issue of the Journal of Materials Research.

BaZrO$_3$ Chemical Synthesis Method Advanced. The
To obtain a refractive index of 1, both the electrical permittivity and the magnetic permeability of a material must be negative. Shalaev and his colleagues demonstrated theoretically that this combination of characteristics can be achieved in the optical range by constructing metallic nanoantennas of the proper length, diameter, and orientation. "The nanoneedles have to be oriented with respect to the incident light and arranged in pairs with the right distance between them," says Shalaev.

"You need to have the right length of needle," he continues. "The length should correspond to half the wavelength of the incident light." For example, to manipulate 1.5-micron light, the nanoantennas should be 0.75 micron in length. Also, the needle diameter must be well within the nanoscale regime (approx. 10 nm) in order to be able to work with optical wavelengths.

The nanoantennas must be fabricated from a highly conductive material, says Shalaev. "The material of choice is silver, or gold," he says. "Copper is also a possibility."

The motion of plasmons, which are essentially a cloud of electrons moving in unison, is behind the unusual properties of the nanoantenna structures. The findings of the Purdue group were published in the March issue of the Journal of Nonlinear Optical Physics and Materials. The paper was authored by Shalaev, Viktor A. Podolský, a postdoctoral fellow at Princeton University, and Andrey K. Sarychev, a senior research scientist at Purdue.

Now that it has been shown theoretically that left-handed nanoantennas can manipulate optical wavelengths, Shalaev speculates that new "20 groups all over the world are trying to demonstrate the technology experimentally." The Purdue team is pursuing this goal as well. Shalaev says that possible fabrication methods for the nanoantenna arrays include chemical synthesis and self-assembly, electron beam lithography, and dip-pen writing.

Shalaev envisions a variety of potential applications for the nanoantenna structures, including optical computing and biological and chemical sensing.

"It turns out that, by employing these plasmonic nanomaterials, you should be able to manipulate light. You can guide light. You can basically simulate all the basic fundamental properties of electronic circuits, but in this case photons start to work," he says.

The anticipated focusing capabilities of nanoantenna structures suggest that "metallic nanostructures might be able to detect even a single molecule of a substance, which is not possible with conventional optics," says Shalaev.

"Left-handed materials might have loads of applications. We don't know yet the full potential of these materials because it's a really new field."
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ENERGY AND ENVIRONMENT

Berkeley Spearheads $3M NanogeoScience Effort

To shepherd the growth of a new field called nanogeochemistry, scientists from Lawrence Berkeley Lab are planning a $3 million nanogeochemistry program that will encompass Berkeley Lab and UC Berkeley.

The program will complement the lab’s Molecular Foundry, a national user facility opening in 2006 that will allow researchers to build and test nanoscale devices.

Glenn Waychunas, a scientist in Berkeley Lab’s Earth Sciences Division, and colleagues Jillian Banfield, Hui-Ying Holman, and Paul Allisato, are spearheading this effort.

To foster improved communication between nanogeochemists worldwide, Waychunas envisions a virtual center that electronically links several institutions that conduct innovative research.

“People who study aerosols don’t talk with people who study oceanic particles who don’t talk with people who study soil particles,” says Waychunas. “We need to bring them together.”

“There is a black hole,” Waychunas continues. “Oceanographers generally study particles that measure 0.2 microns and larger, which means a lot of nanoscale particles are not examined, particularly with respect to formation mechanisms.”

As a start, 85 researchers from almost 30 universities, federal agencies, and national labs convened at Berkeley Lab for three days this past summer and mapped what is and isn’t known in nanogeochemistry. In addition to bringing nanogeochemists under one roof for the first time, the workshop was tasked with helping federal agencies decide how to best facilitate research. The attendees collated important, underfunded research opportunities into a report that will be presented to several federal agencies later this year.

Among these research opportunities is learning how oceans capture atmospheric carbon, a complex process that plays a key role in our understanding of climate change. On land, researchers are studying how nanoscale minerals capture toxins such as arsenic, copper, and lead from the soil. Facilitating this process, called soil

tics using nanoparticles, the inventors say the fabrication of optical plastic parts with temperature-stable optical properties—without sacrificing important processing characteristics—has been an elusive goal.

To produce a nanocomposite with enhanced refractive index (n) stability with respect to temperature (T), the inventors propose dispersing nanoscale particles that have a value of dn/dT that is directionally opposed (of opposite sign) to that of the polymeric host material. In one example presented in the patent, magnesium oxide nanoparticles of approx. 10 nm in size were compounded into polymethylmethacrylate. Lenses were molded from the pellets produced from compounding. The inventors report in the patent that the resulting dispersion of the nanoparticles in the lenses was quite good when examined under the scanning electron microscope.

Samsung Li-Battery Design Uses Nanotubes. Engineers from Samsung SDI Co., Ltd. (Suwon, KR) have developed a carbon nanotube-based negative active material for a lithium secondary battery. The active material is composed of a crystalline or amorphous carbon core, a catalyst layer formed on the core, and carbon vapor-grown fibers or carbon nanotubes. The Samsung scientists claim in U.S. Patent 6,440,810 that such carbon nanotubes or fibers form a fine path between neighboring active materials, thereby improving the con-