Extraordinarily transparent compact metallic metamaterials

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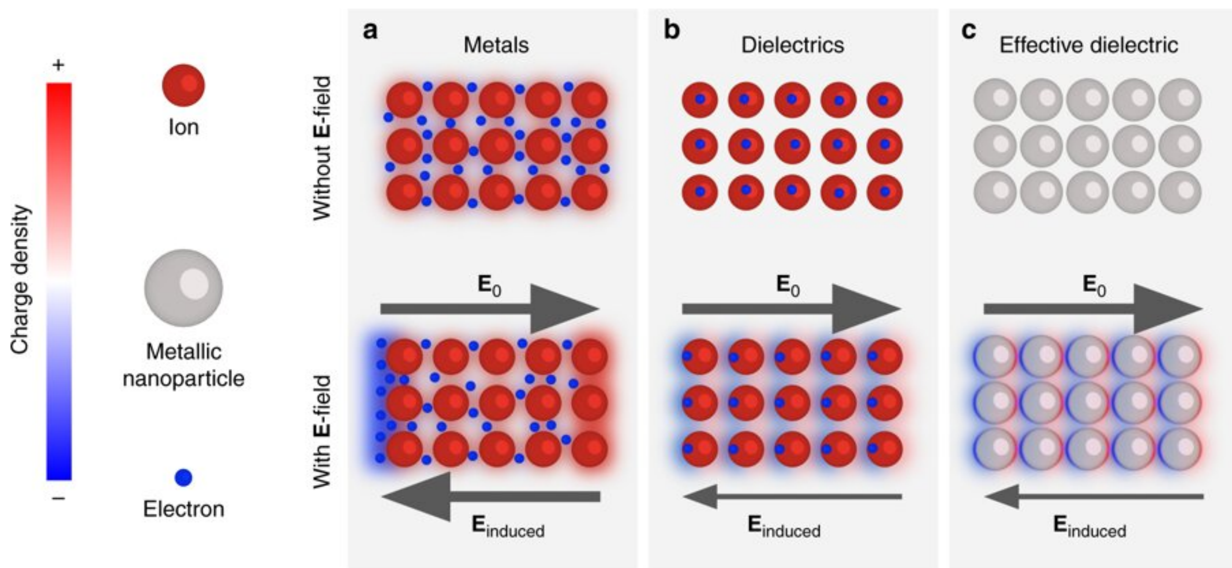


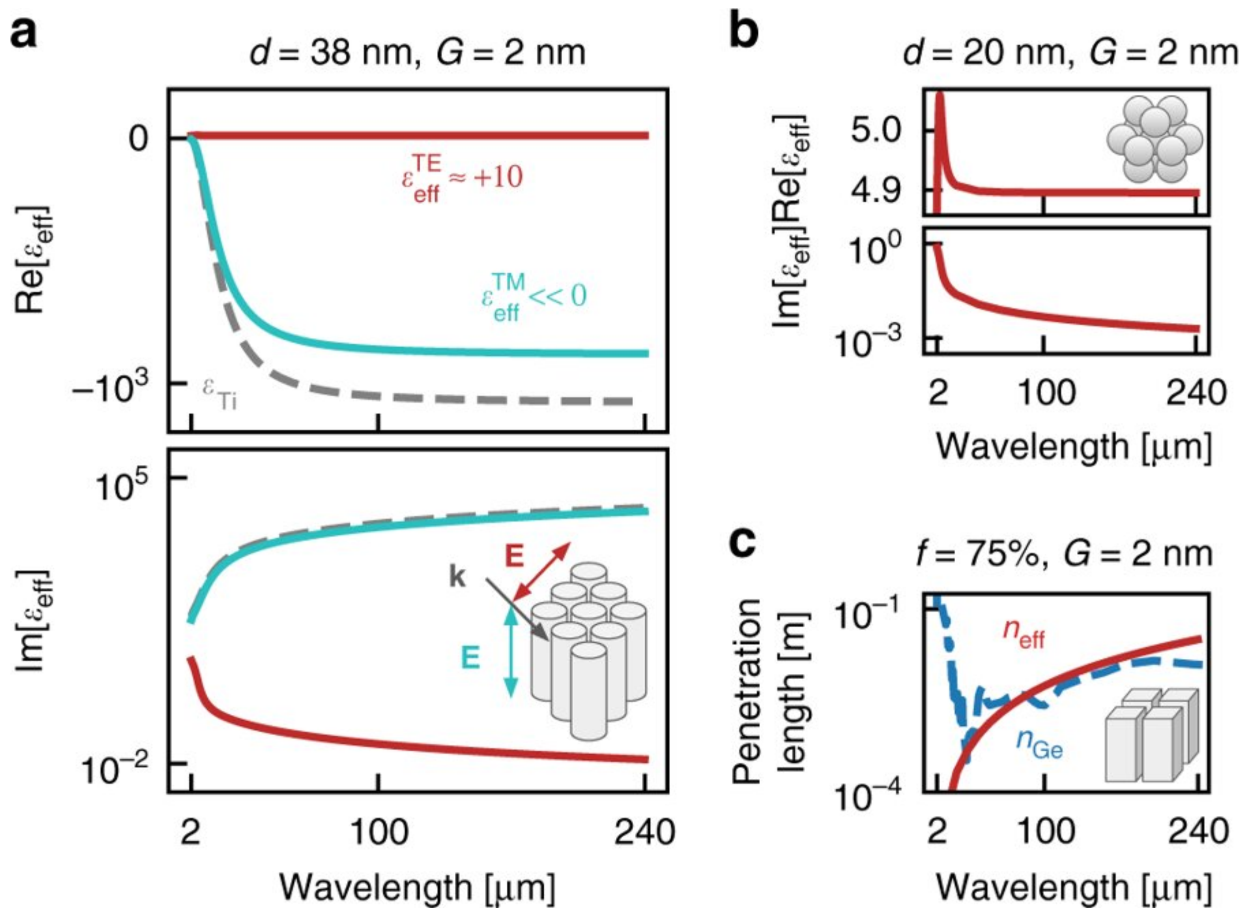
An illustration of how metals, dielectrics, and effective dielectrics respond to a slowly varying electric field. Within in each system, the applied field is opposed by an induced electric field generated by the buildup of surface charges. (a) In metals, the electrons are free to move until the applied and induced fields cancel in the bulk. In dielectrics (b) and effective dielectrics (c), the surface charge is generated by the polarization of the (meta-)atoms or (meta-)molecules, and the induced field is weaker than the applied field. Credit: Nature Communications, doi: 10.1038/s41467-019-09939-8

In materials science, achromatic optical components can be designed with high transparency and low dispersion. Materials scientists have shown that although metals are highly opaque, densely packed arrays of metallic nanoparticles with more than 75 percent metal by volume can become more transparent to infrared radiation than dielectrics such as germanium. Such arrays can form effective dielectrics that are virtually dispersion-free across ultra-broadband ranges of wavelengths to engineer a variety of next-generation metamaterial-based optical devices.

Scientists can tune the local refractive indices of such materials by altering the size, shape and spacing of nanoparticles to design gradient-index lenses that guide and focus light on the microscale. The electric field can be strongly concentrated in the gaps between metallic nanoparticles for the simultaneous focusing and 'squeezing' of the dielectric field to produce strong, doubly enhanced hotspots. Scientists can use these hotspots to boost measurements made using infrared spectroscopy and other non-linear processes across a broad frequency range.

In a recent study now published in *Nature Communications*, Samuel J. Palmer and an interdisciplinary research team in the departments of Physics, Mathematics and Nanotechnology in the U.K., Spain and Germany, showed that artificial dielectrics can remain highly transparent to infrared radiation and observed this outcome even when the particles were nanoscopic. They demonstrated the electric field penetrates the particles (rendering them imperfect for conduction) for strong interactions to occur between them in a tightly packed arrangement. The results will allow materials scientists to design optical components that are achromatic for applications in the mid-to-infrared wavelength region.

Palmer and colleagues were able to tune the local refractive index of these components by altering the size, shape and spacing of nanoparticles with sensitivity to the local refractive index of the surrounding environment. The scientists enhanced the electric field in the gaps between the metallic nanoparticles in the array and simultaneously exploited their transparency, tunability and high metallic filling fraction to design a gradient-index lens. The work focused light on the microscale and squeezed the electric field in the nanoscale to produce the doubly enhanced electric field hotspot throughout the infrared (IR) region. The scientists envision that the new work will boost measurements made using IR spectroscopy and other nonlinear processes across a broad-range of frequencies.



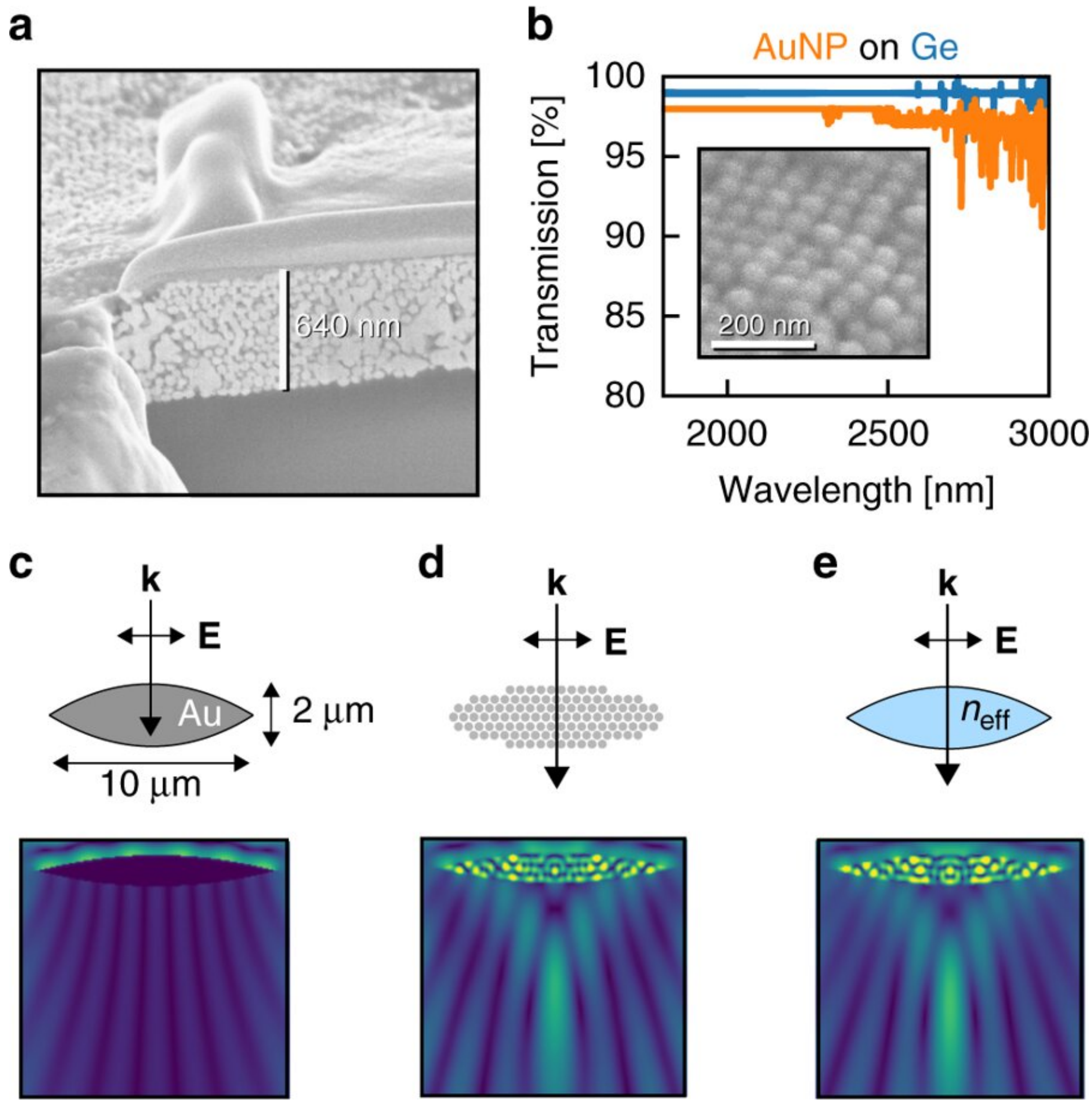
Effective permittivity of metallic nanoparticle arrays. (a) The effective permittivity of an array of titanium nanocylinders (with diameter d = 38 nm and surface-to-surface separation G = 2 nm) for TE (red curve) and TM (blue curve) polarized light compared to the permittivity of solid titanium (dashed curve). (b)

The effective permittivity of titanium nanospheres, (d = 20 nm, G = 2 nm) for unpolarized light. (c) The effective penetration length of the nanoparticle arrays can exceed that of real dielectrics, such as germanium, even for metallic filling fractions as high as 75 percent. Credit: Nature Communications, doi: 10.1038/s41467-019-09939-8

Materials scientists are presently able to develop new and advanced materials; however, no new material is truly homogenous in its constitution. Nevertheless, most materials can be characterized using homogenous microscopic properties such as refractive indices wherein the atomistic inhomogeneities are smaller than the average wavelengths of optical light incident on the material. Artificially constructed materials known as metamaterials are described by an effective index when the material contains a sufficiently subwavelength structure. Early metamaterials included artificial dielectrics composed of centimeter-scale arrays of metallic particles capable of guiding and focusing radio waves like a dielectric. The metallic particles of early artificial dielectric materials were so large they behaved as perfect conductors with high transparency to radio waves. Recent research in materials science aims to build effective dielectrics for the visible and infrared spectrum using nanoscale metallic particle arrays. Advances in the assembly of metallic nanoparticles can then allow for sophisticated engineering of unprecedented light-matter interactions in the optical domain.

In the present work, Palmer et al. contrasted the transparency of nanocylinder arrays and nanospheres (although nanoparticles can have other shapes) to germanium in order to demonstrate that the arrays could guide and focus light. The arrays of nanocylinders behaved as effective dielectrics with transverse electric polarized light; where a transverse force on the electrons led to oscillating surface charges that mimicked the oscillating dipoles of an atom in a real dielectric.

In contrast, the response of the cylinders to transverse magnetic polarized light was similar to the bulk metal, since electrons were free to move under the action of the longitudinal electric field without encountering the cylinder surfaces. The arrays of nanospheres in the study behaved as effective dielectrics, regardless of the incident polarization—focusing the electrons in any direction to result in surface charges that imitated the oscillating dipoles of a dielectric. Such arrays showed high transparency compared to real dielectrics such as germanium—even when the system had higher than 75 percent metal.



Experimental and numerical demonstrations of transparent metallic arrays. (a) Microscopy image of 60 nm diameter gold colloidal supercrystal deposited on a Ge substrate. (b) The metallic particles show high infrared transparency. (c–e) The effective dielectrics are transparent enough to act as micrometer-scale lenses to infrared radiation of wavelength λ0 = 2 μm, as shown by the magnetic near-fields. There is good agreement between (d) the full geometry of titanium cylinders with diameter 38 nm and surface-to-surface gap 2 nm and (e) the homogenized geometry, neff = 3.2 + 0.5i. Credit: Nature Communications, doi:

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To test the accuracy of the proposed theory, Palmer et al. produced a highly ordered colloidal supercrystal using gold nanoparticles of 60 nm diameter. They deposited the supercrystal on a germanium substrate and characterized the material (tested physical properties) using a UV-vis-NIR spectrophotometer. The scientists observed outstanding transparency of the materials, demonstrating the feasibility of experimentally producing metamaterials. Using magnetic near-fields, they showed that the effective dielectrics were transparent enough to act as micrometer-scale lenses to infrared radiation. Despite containing 82 percent metal by volume, the scientists observed that breaking the solid gold into an array of gold nanocylinders produced a transparent lens capable of focusing light, closely resembling the behavior of a homogenous dielectric lens.

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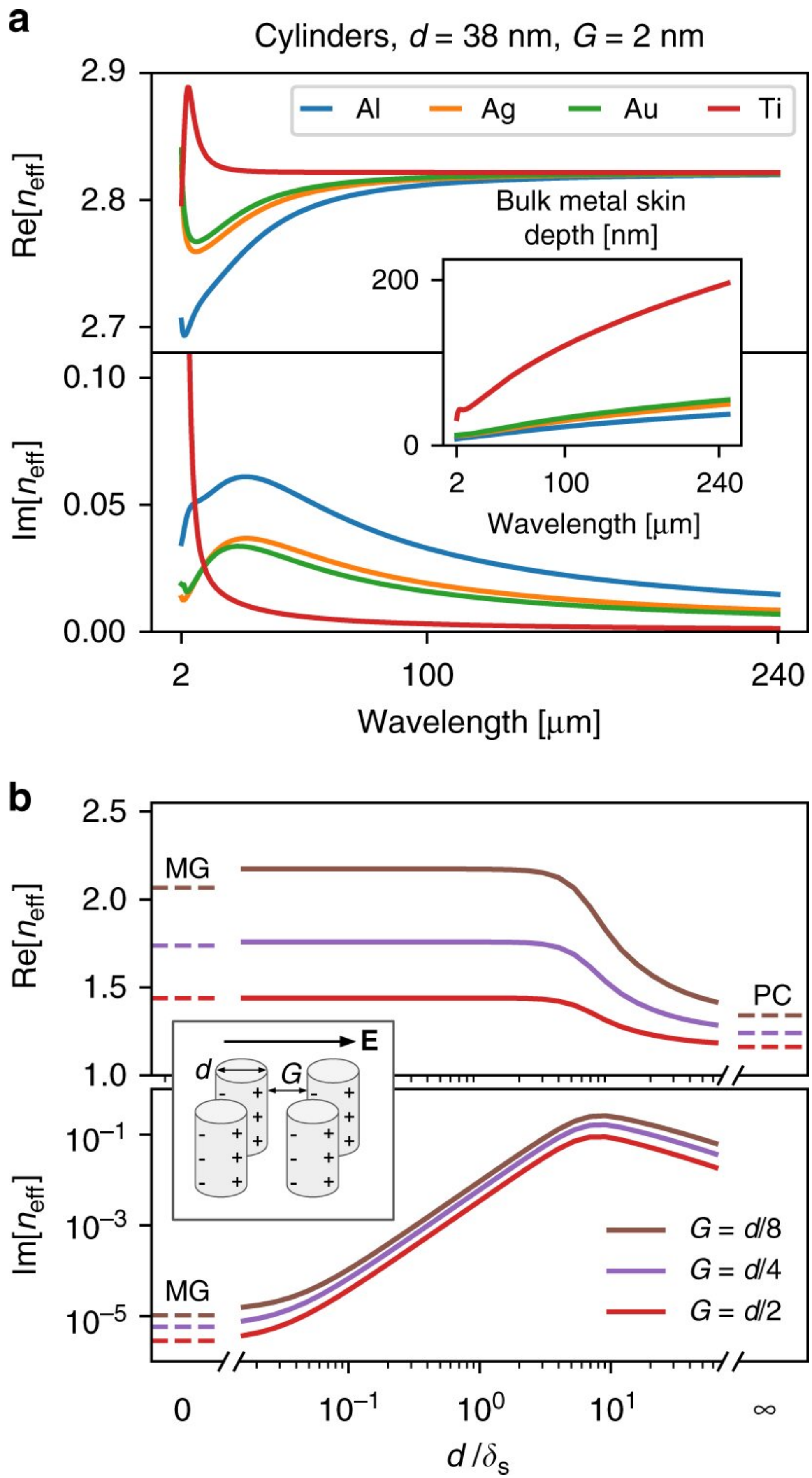
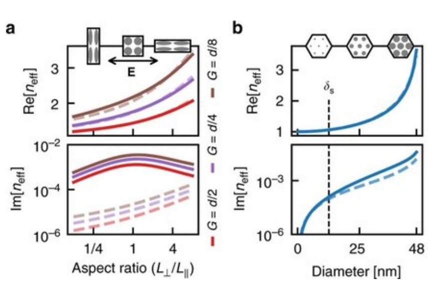


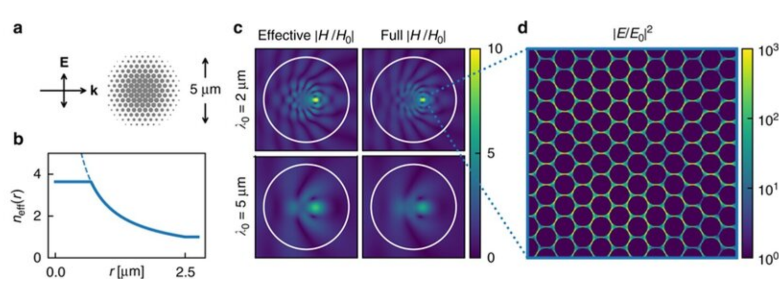
a
Cylinders, d = 38 nm, G = 2 nm
Al
Ag
Au
Ti
Re[n_eff]
Im[n_eff]
Bulk metal skin depth [nm]
Wavelength [μm]
b
MG
PC
E
d
G
G = d/8
G = d/4
G = d/2
d / δ_s

Transparency as a function of material skin depth. (a) The effective index of a square array of nanocylinders, composed of aluminum, gold, silver, and titanium. Inset: the skin depth of each metal, calculated using the Lorentz–Drude model of permittivity. (b) At a fixed wavelength, it is the ratio of the particle diameter to the skin depth of the metal that determines whether the particles behave as quasi-static dipoles or perfect conductors. The effective index is remarkably constant for d ≲ δs. Credit: Nature Communications, doi: 10.1038/s41467-019-09939-8

The scientists then compared different types of metals (aluminum, silver, gold and titanium) to show that materials with longer skin depths produced the most transparent and least dispersive nanoparticle arrays. Palmer et al. showed that at a fixed wavelength, the ratio of the particle diameter to the skin depth of the metal determined if the particle would behave as quasiparticle dipoles or as perfect conductors.

In addition to high transparency, the scientists could tune the system by controlling the size, shape and space of the particles. For instance, Palmer et al. controlled the aspect ratio of arrays of elliptical cylinders to show that the anisotropic response of the material could be tuned. The numerical results showed that the effective index could be easily tuned to vary by more than 50 percent when the system was rotated. Thereby the scientists were able to tune the effective index by fixing the particle positions and tuning their sizes.





LEFT: The effective index of gold nanocylinders as functions of aspect ratio and particle size. Numerics (solid lines) and Maxwell Garnett mixing formula (dashes). (a) The aspect ratios of square arrays of cylinders were varied, while keeping the volume and surface-to-surface separation of each cylinder constant, as shown in the insets. The undistorted diameter of the cylinders was d = 30 nm and the incident wavelength was λ0 = 200 µm. (b) The cylinders were placed on a triangular lattice of length 50 nm, and their diameters were varied from 0 nm ≤ d ≤ 48 nm for an incident wavelength of λ0 = 2 µm. RIGHT: Designing a gradient-index lens with 'doubly-enhanced' hotspots. (a) Schematic of a 'concentrator' gradient-index lens composed of gold nanocylinders on a triangular lattice with 50 nm site-to-site separation. (b) Effective index profile of the concentrator lens, ideal (dashed) and achieved (solid). (c) Magnetic near-fields calculated using the effective geometry and the full geometry both confirm that plane waves are focused towards the origin of the lens. (d) Within the focal point of the lens, the combined focusing and squeezing of the electric field produces 'doubly-enhanced' hotspots. Credit: Nature Communications, doi: 10.1038/s41467-019-09939-8

To highlight this potential to tune the local effective index, Palmer et al. then constructed a gradient-index (GRIN) lens using triangular lattices of gold cylinders and varied the diameters of the cylinders with position. Using the GRIN lens, the scientists were able to simultaneously focus light on the microscale and then 'squeeze' light on the nanoscale to produce the intense, 'doubly enhanced' electric field hotspots. Unlike plasmonic enhancements, the effect did not rely on lossy resonances, demonstrating broadband and low-loss properties.

They showed that the focal point of the GRIN lens had to coincide with the region of closest packing to maximize squeezing of the electric field. Unlike magnetic fields that were continuous across the air-metal interfaces in the study, the electric field strongly localized in the gaps.

As a result, squeezing a 2 μm wavelength into 2 nm gaps produced strong hotspots of high intensity in the study.

In this way, Palmer et al. constructed low-loss, effective dielectrics from arrays of metallic nanoparticles. The scientists obtained highly transparent arrays that exceeded the transparency of real dielectrics such as germanium; renowned for their transparency to low energy radiation. They were also able to locally tune and control the size, shape and space of the particles forming the new metamaterials. The scientists showed the effective index to be essentially constant for all wavelengths greater than 2 μm. This work will allow materials scientists to design and engineer sophisticated optical devices with metamaterials that guide or enhance light across a broad range of frequencies, essentially without an upper bound on wavelength.

More information: Samuel J. Palmer et al. Extraordinarily transparent compact metallic metamaterials, *Nature Communications* (2019). DOI: 10.1038/s41467-019-09939-8

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