

Physicists demonstrate quantum plasmons in atomic-scale nanoparticles

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Addressing a half-century-old question, engineers at Stanford have conclusively determined how collective electron oscillations, called plasmons, behave in individual metal particles as small as just a few nanometers in diameter. This knowledge may open up new avenues in nanotechnology ranging from solar catalysis to biomedical therapeutics.

The [physical phenomenon](#) of plasmon resonances in small [metal particles](#) has been used for centuries. They are visible in the vibrant hues of the great stained-glass windows of the world. More recently, plasmon resonances have been used by engineers to develop new, light-activated cancer treatments and to enhance [light absorption](#) in [photovoltaics](#) and photocatalysis.

"The stained-glass windows of Notre Dame Cathedral and Stanford Chapel derive their color from metal nanoparticles embedded in the glass. When the windows are illuminated, the nanoparticles scatter specific colors depending on the particle's size and geometry " said Jennifer Dionne, an assistant professor of [materials science and engineering](#) at Stanford and the senior author of a new paper on plasmon resonances to be published in the journal *Nature*. In the study, the team of engineers report the [direct observation](#) of plasmon resonances of individual metal particles measuring down to one nanometer in diameter—just a few atoms across.

"For particles smaller than about ten nanometers in diameter, plasmon resonances are poorly understood," said Jonathan Scholl, a doctoral

candidate in Dionne's lab and first author of the paper. "This class of quantum-sized metal nanoparticles has been largely under-utilized. Exploring their size-dependent nature could open up some interesting applications at the nanoscale."

Longstanding debate

The science of tiny metal particles has perplexed physicists and engineers for decades. Below a certain threshold, as metallic particles near the quantum scale —about 10 [nanometers](#) in diameter — classical physics breaks down. The particles begin to demonstrate unique physical and chemical properties that bulk counterparts of the very same materials do not. A nanoparticle of silver measuring a few atoms across, for instance, will respond to photons and electrons in ways profoundly different from a larger particle or slab of silver.

By clearly illustrating the details of this classical-to-quantum transition, Scholl and Dionne have pushed the field of plasmonics into a new realm that could have lasting consequences for catalytic processes such as artificial photosynthesis, cancer research and treatment, and quantum computing.

"Particles at this scale are more sensitive and more reactive than bulk materials," said Dionne. "But we haven't been able to take full advantage of their optical and electronic properties without a complete picture of the science. This paper provides the foundation for new avenues of nanotechnology entering the 100-to-10,000 atom regime."

Noble metals

In recent years, engineers have paid particular attention to nanoparticles of the noble metals: silver, gold, palladium, platinum and so forth. These

metals are well known to support localized surface plasmon resonances, the collective oscillations of electrons at the metal surface in response to light or an electric field.

Other important physical properties can be further driven when plasmons are constrained in extremely small spaces, like the nanoparticles Dionne and Scholl studied. The phenomenon is known as quantum confinement.

Depending on the shape and size of the particle, quantum confinement can dominate a particle's electronic and optical response. This research allows scientists, for the first time, to directly correlate a quantum-sized plasmonic particle's geometry—its shape and size—with its plasmon resonances.

Standing to benefit

Nanotechnology stands to benefit from this new understanding. "We might discover novel electronic or photonic devices based on excitation and detection of plasmons in quantum-sized particles. Alternatively, there could be opportunities in [catalysis](#), quantum optics, and bio-imaging and therapeutics," said Dionne.

Medical science, for instance, has devised a way to use nanoparticles excited by light to burn away cancer cells, a process known as photothermal ablation. Metal nanoparticles are affixed with molecular appendages called ligands that attach exclusively to chemical receptors on cancerous cells. When irradiated with infrared light, the metal nanoparticles heat up, burning away the cancerous cells while leaving the surrounding healthy tissue unaffected. The properties of smaller nanoparticles might improve the accuracy and the effectiveness of such technologies, particularly since they can be more easily integrated into cells.

There is great promise for such small nanoparticles in catalysis, as well. The greater surface-area-to-volume ratios offered by atomic-scale nanoparticles could improve water-splitting and artificial photosynthesis, yielding clean and renewable energy sources from artificial fuels. Taking advantage of quantum plasmons in these metallic nanoparticles could significantly improve catalytic rates and efficiencies.

Aiding and abetting

The researchers' ability to observe plasmons in particles of such small size was abetted by the powerful, multi-million dollar environmental scanning transmission electron microscope (E-STEM) installed recently at Stanford's Center for Nanoscale Science and Engineering, one of just a handful of such microscopes in the world.

E-STEM imaging was used in conjunction with electron energy-loss spectroscopy (EELS) — a research technique that measures the change of an electron's energy as it passes through a material — to determine the shape and behavior of individual [nanoparticles](#). Combined, STEM and EELS allowed the team to address many of the ambiguities of previous investigations.

"With the new microscope, we can resolve individual atoms within the nanoparticle," said Dionne, "and we can directly observe these particles' quantum plasmon resonances."

Ai Leen Koh, a research scientist at the Stanford Nanocharacterization Laboratory, and co-author of the paper, noted: "Even though plasmons can be probed using both light and electrons, electron excitation is advantageous in that it allows us to image the nanoparticle down to the atomic level and study its plasmon resonances at the same time."

Scholl added, "Someday, we might use the technique to watch reactions

in progress to better understand and optimize them."

Elegant and versatile

The researchers concluded by explaining the physics of their discovery through an elegant and versatile analytical model based on well-known quantum mechanical principles.

"Technically speaking, we've created a relatively simple, computationally light model that describes plasmonic systems where classical theories have failed," said Scholl.

Their elegant and versatile model opens up numerous opportunities for scientific gain.

"This paper represents fundamental research. We have clarified what was an ambiguous scientific understanding and, for the first time, directly correlated a particle's geometry with its plasmonic resonance for quantum-sized [particles](#)," summarized Dionne. "And this could have some very interesting, and very promising, implications and applications."

Provided by Stanford University

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