Chemicals induce dipoles to damp plasmons

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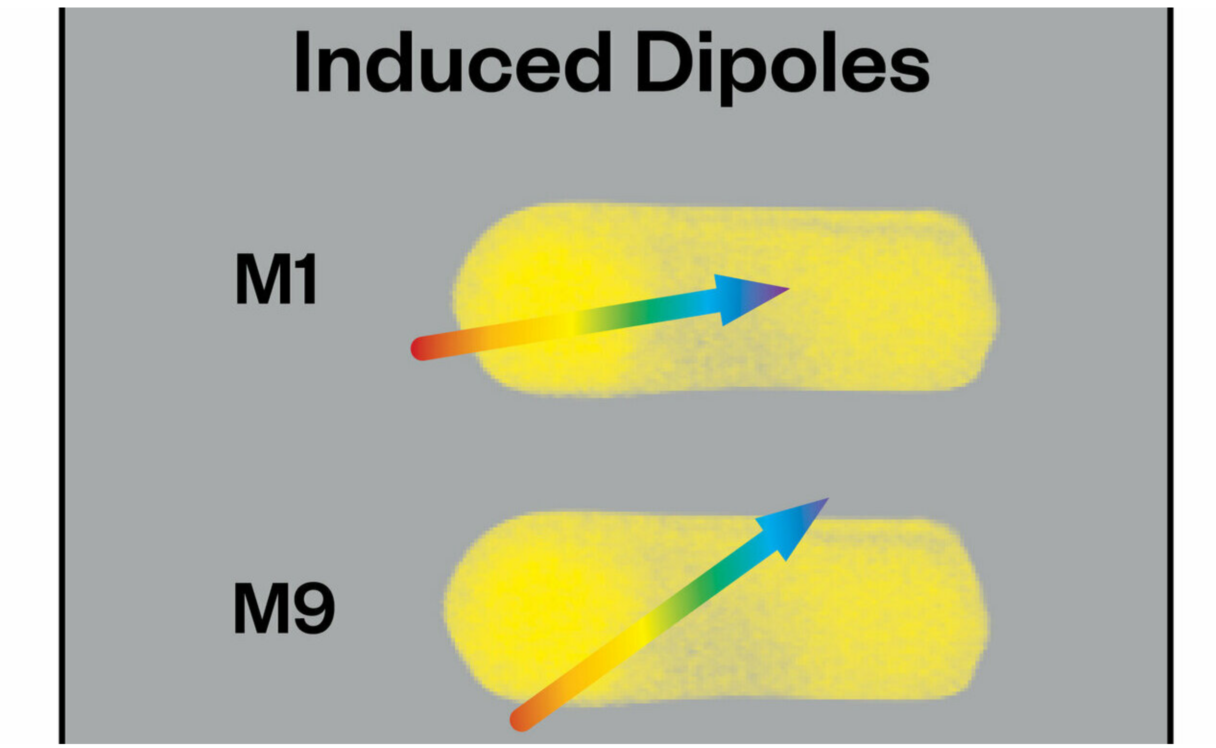

Illustration shows the process of using dipoles induced by specific molecules to measure their damping effect on gold nanoparticle plasmons. Credit: Alese Pickering/Rice University

The light scattered by plasmonic nanoparticles is useful, but some of it gets lost at the surface and scientists are now starting to figure out why.

In novel experiments at Rice University and the Johannes Gutenberg University of Mainz, along with theoretical work at Princeton

University, researchers found that molecules placed on the surface of a single gold nanorod affect its plasmonic response by altering the electronic structure of the particle itself.

The finding could enhance applications like catalysis that involve plasmon-driven chemistry.

Plasmons are ripples of electrons that resonate across the surface of a metal nanoparticle when triggered by light. The light they receive at one wavelength, or color, is radiated at the same wavelength, and that can inform researchers about the particle and its environment.

Surface plasmons help sense the presence of chemicals, enable photochemistry and selectively catalyze chemical reactions. But light lost between the particle's surface and the researcher's eye can contain additional information previously not considered.

It had been thought signal loss via plasmon damping was due to chemicals adsorbed to the nanoparticle surface, perhaps through charge transfer from the metal to the chemical substances. But Stephan Link, a professor of chemistry and of electrical and computer engineering at Rice, had doubts that just one explanation would fit all studies.

They led Link, lead author Benjamin Förster and their colleagues to the discovery of an entirely different mechanism, reported this week in *Science Advances*.

Their strategy was to put two types of identically sized molecules with different atomic arrangements onto single gold nanorods for analysis. These molecules, cage-like carborane thiols, induced surface dipoles in the metal that in turn scattered enough of the plasmons' energy to damp their signal.

That let the researchers see and measure damping directly with no interference from other molecules or other nanorods. The proximity of the thiols, identical except for the placement of one carbon atom, to the nanorod induced unique dipole moments—the molecules' positive and negative poles that change strength and move like the needle of a compass—on the metal surface.

Emily Carter, a theoretical-computational scientist and dean of the School of Engineering and Applied Science at Princeton, performed detailed quantum mechanical calculations to test mechanisms that could explain the experiments.

"Plasmonic resonances have a spectral width that, together with resonance wavelengths, gives specific colors," Link said. "A narrow line gives you a truer color. So we looked at how the width of this resonance changes when we put molecules on the particle."

Not just any molecules would do. The carborane thiols, molecules of the exact same size, stick to gold nanoparticles in equal measure but are chemically different enough to change the plasmons' spectral width. That let the researchers measure plasmon damping by each type of molecule without interference from other damping mechanisms.

The plasmons that flow across a surface depend so heavily on the particle's size and shape that little attention had been paid to the effect of chemicals adsorbed to the surface, Förster said.

"If you change the surface of the nanorod, the energy gets lost in different ways," he said. "We didn't understand this at all. But if something loses energy, it's not functioning as you want it to function."

The refractive properties of the surrounding medium and averaging of signals from multiple particles of various size and shape can also affect the signal. That had also made it difficult to analyze the impact of adsorbed chemicals.

"Several contributions determine the plasmon resonance width," Link said. "But there's a fudge factor everybody invokes that nobody had really tackled in a quantitative way. A lot of people blamed charge transfer, meaning excited hot electrons moved from the metal to the molecule.

"We are saying that's not the case here," he said. "It may not be the same every time you put a molecule on a metal particle, but this gives us, for the first time, a complete quantitative study that also doesn't turn a blind eye to the chemistry at the interface. It lets us understand that the chemistry is important.

"The work is fundamental and I think it's pretty because it's so simple," Link said. "We combined the right sample, the experiment and single-particle spectroscopy with advanced theory, and we put it all together."

More information: "Plasmon damping depends on the chemical nature of the nanoparticle interface" *Science Advances* (2019). DOI: 10.1126/sciadv.aav0704 ,
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