

## NEWS &amp; VIEWS

## SPECTROSCOPY

# Expanding versatility

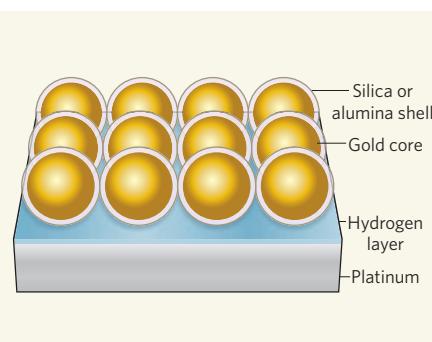
Martin Moskovits

**Gold nanoparticles coated with a thin layer of an oxide allow molecules adsorbed on surfaces as diverse as those of platinum, yeast cells or citrus fruits to be characterized routinely in the laboratory.**

Placing molecules on properly nanostructured substrates is a crucial part of the working principle of surface-enhanced Raman spectroscopy (SERS), a technique that is widely used to characterize the chemical composition of a sample. This approach has been shown to boost the intensity of the molecules' vibrational Raman spectrum by factors exceeding one million<sup>1</sup>, and has allowed a single molecule to be detected under favourable circumstances<sup>2,3</sup>. One drawback of SERS is that the Raman signal, obtained by scattering laser light from the sample, is sufficiently strong only for molecules residing on gold or silver (or hard-to-handle metals such as lithium or sodium) substrates that have roughened surfaces or consist of arrangements of metallic nanoscale features. On page 392 of this issue, Li *et al.*<sup>4</sup> describe an innovative approach to SERS, termed shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), that expands the versatility of SERS.

The enhancement of the Raman signal that distinguishes SERS from other spectroscopic techniques arises from collective electron excitations called surface plasmons that form at the nanostructured substrate's surface when light strikes the sample. Such a plasmonic resonance helps to concentrate the intensity of both the incident light and the Raman radiation scattered by the sample in features such as nanometre-sized clefts and crannies in the underlying substrate<sup>5–8</sup>. Since its first demonstration more than 30 years ago<sup>1</sup>, SERS has become an active field of research and, along the way, has spawned the more general field of plasmonics<sup>9,10</sup> and metamaterials<sup>11</sup>.

Li and colleagues' SHINERS technique<sup>4</sup> relies on coating nanoparticles with a very thin layer of an oxide, such as silica or alumina, and then spreading these nanoparticles onto a sample. For a layer of hydrogen on a single-crystal platinum surface (Fig. 1), the authors were able to record intense SHINERS Raman spectra of the vibrational modes of the hydrogen at this interface. Next, and to investigate the applicability of SHINERS to non-metallic surfaces, they measured the Raman spectrum of a single-crystal silicon wafer covered with hydrogen. Finally, to demonstrate the versatility of



**Figure 1 | Spectroscopy with oxide-gold nanoparticles.** Li and colleagues<sup>4</sup> show that, if gold nanoparticles coated with a thin layer of an oxide (silica or alumina) are arrayed on a sample such as a single-crystal platinum surface covered by a layer of hydrogen, they act as an amplifier to the intensity of light scattered by the sample when light is shone on it. Such an approach allows the application of surface-enhanced Raman spectroscopy — a form of spectroscopy that is usually limited to probing the vibrational frequencies of substances residing on gold or silver substrates — to be expanded to many other substrates.

their technique, they applied it to biological systems and food. They report seeing new vibrational bands in the Raman spectrum of yeast cells — presumably due to biomolecules that reside in the cells' surface. They also detected the potent insecticide parathion by spreading the silica-coated nanoparticles on the skin of a parathion-contaminated orange.

Essentially, what Li *et al.* have invented is a 'powder' with which one can dust a sample to detect and identify the molecules at its surface. Researchers have previously attempted to extend the applicability of SERS to various materials and substrate morphologies by using approaches similar to that used by the authors<sup>4</sup>. The late SERS pioneer Michael Weaver recorded Raman spectra from molecules adsorbed on transition metals by depositing thin layers of those metals on nanostructured gold or silver substrates, while ensuring that the thickness of the layer would not damp out the gold's strong plasmonic resonance too much<sup>12</sup>. Likewise, glass-coated

silver and gold nanoparticles have been used broadly<sup>13</sup> and even commercialized.

But Li and colleagues' insight of making the silica coat so thin as to increase the plasmonic influence of its golden core on the sample under investigation as much as possible, while avoiding direct contact of the sample with the core, is new and potentially powerful. And, as the authors have demonstrated, it is especially useful in revealing the Raman spectra of molecules adsorbed onto metals through the creation of a hot spot — a tiny volume in which the optical electromagnetic fields are especially concentrated — at the junction between the silica-coated nanoparticle and the adsorbate/substrate.

One feature that will have to be clarified in future work is the extent to which molecules interacting nonspecifically with a substrate — as parathion molecules do with orange peel — migrate from the substrate to the silica-coated gold nanoparticles. In this situation, it would be the hot spot between neighbouring nanoparticles that produces the Raman signal, as opposed to that between the nanoparticles and the substrate. But such details will be elucidated as SHINERS is put to use in the materials and life sciences. ■

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