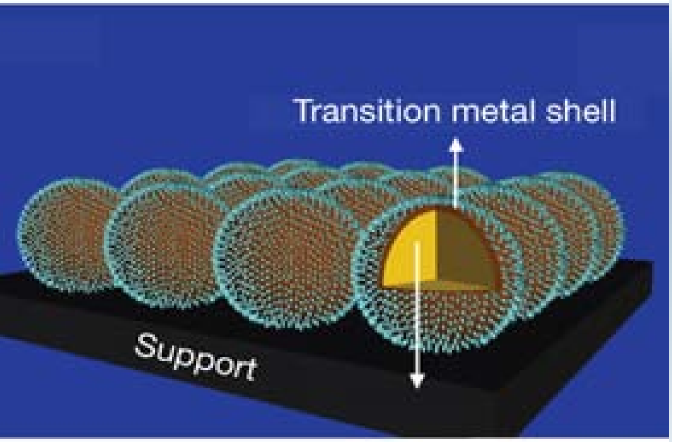
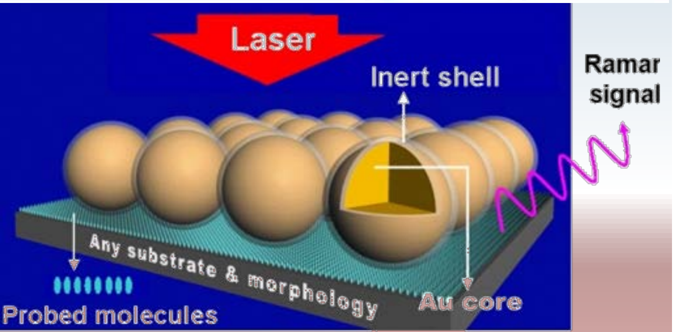
Shell-isolated nanoparticle-enhanced Raman spectroscopy





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Surface-enhanced Raman scattering (SERS)

❖ Surface Enhanced Raman Scattering (SERS) has long been used to enhance weak Raman signals by means of surface plasmon resonance using nanoscale colloidal particles or rough metallic substrates, allowing detection of chemical species at parts per million (ppm) levels.

❖ Generally substrates based on metals such as Ag, Au and Cu, either with roughened surfaces or in the form of nanoparticles, are required to realise a substantial SERS effect, and this has severely limited the breadth of practical applications of SERS.

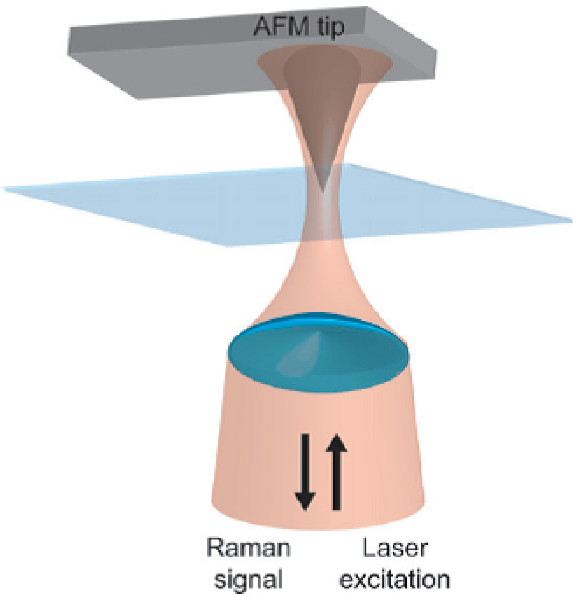
Tip-enhanced Raman spectroscopy (TERS)

❖ The TERS method is based on the combination of Raman, SERS and AFM, where a nanoscale gold tip above the substrate acts as the Raman signal amplifier.

❖ Since the AFM tip is on the nanometer scale, it is possible to obtain localized enhancement on the same scale.

❖ A robust technique for rapid chemical imaging with nanometer spatial resolution.

❖ The drawback is that the total Raman scattering signal from the tip area is rather weak, thus limiting TERS studies to molecules with large Raman cross-sections.



Only the area of the sample in contact with the tip experiences enhancement.

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Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS)

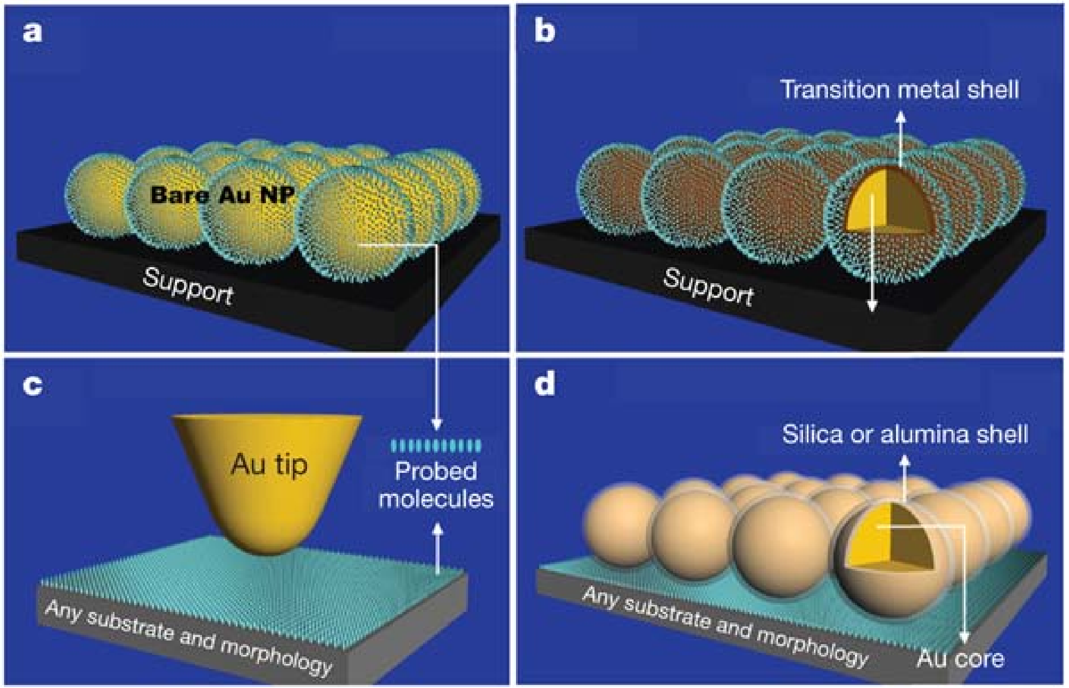
❖ The Raman signal amplification is provided by Au NPs with an ultrathin silica or alumina shell.

❖ A monolayer of such nanoparticles is spread as ‘smart dust’ over the surface that is to be probed.

❖ Each nanoparticle acts as an Au tip in the TERS system, and thus this technique simultaneously brings thousands of TERS tips to the substrate surface to be probed.

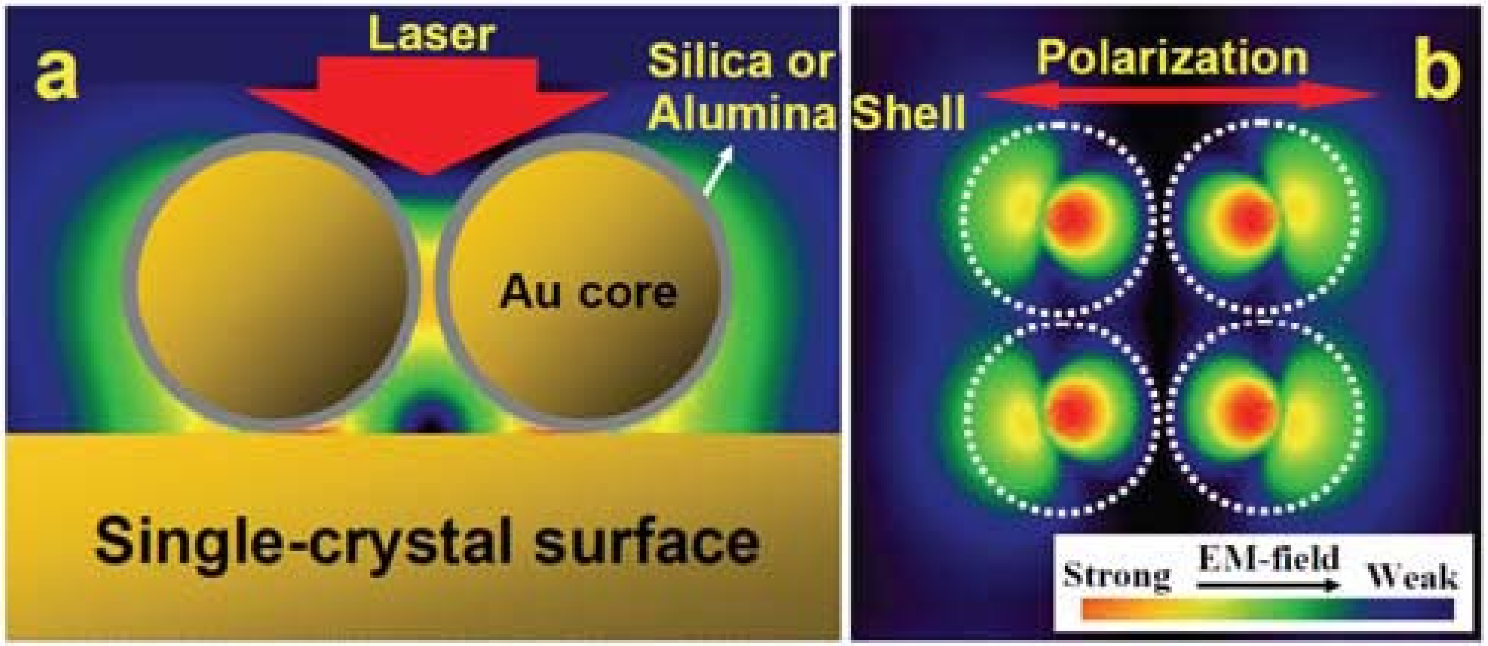
❖The ultrathin coating keeps the nanoparticles from agglomerating, separates them from direct contact with the probed material.

The working principles of SHINERS compared to other modes.



(a) Bare Au nanoparticles: contact mode.
(b) Au core–transition metal shell nanoparticles adsorbed by probed molecules: contact mode.
(c) Tip-enhanced Raman spectroscopy: noncontact mode.
(d) SHINERS: shell-isolated mode.

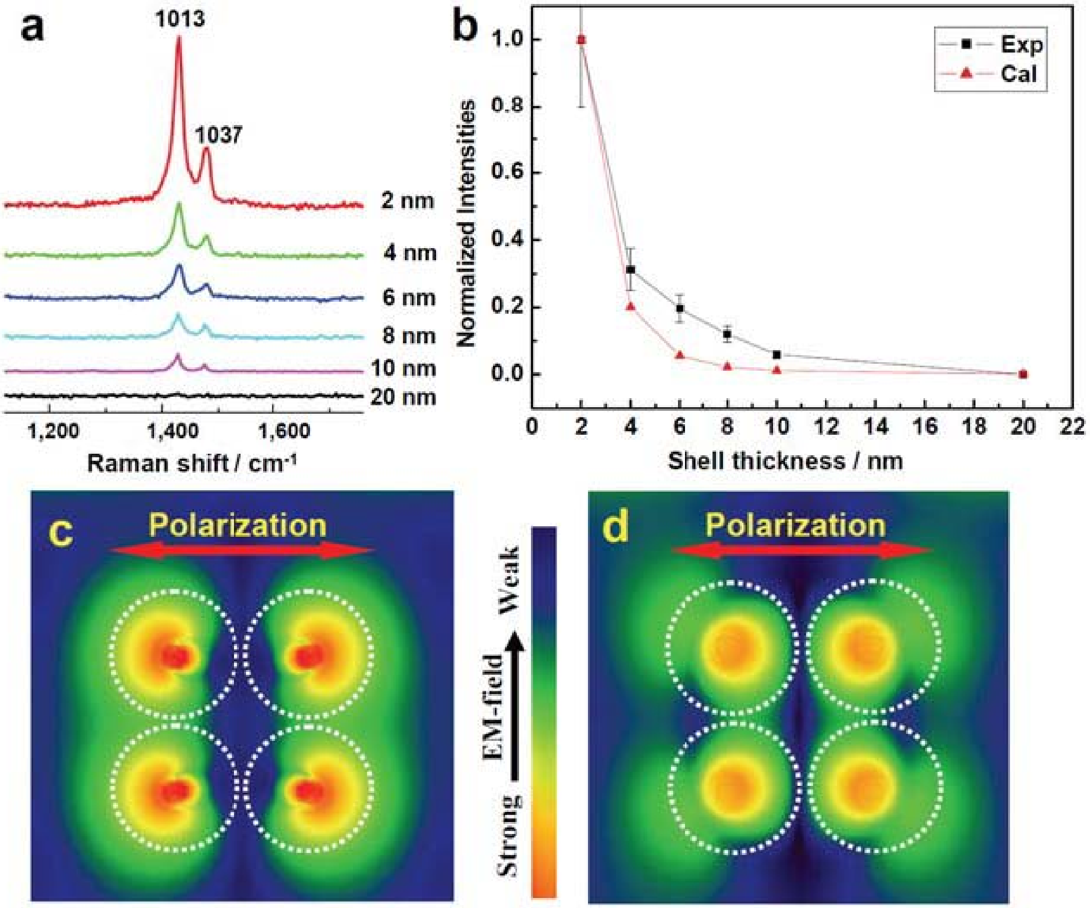
FDTD simulation of the field-enhancement



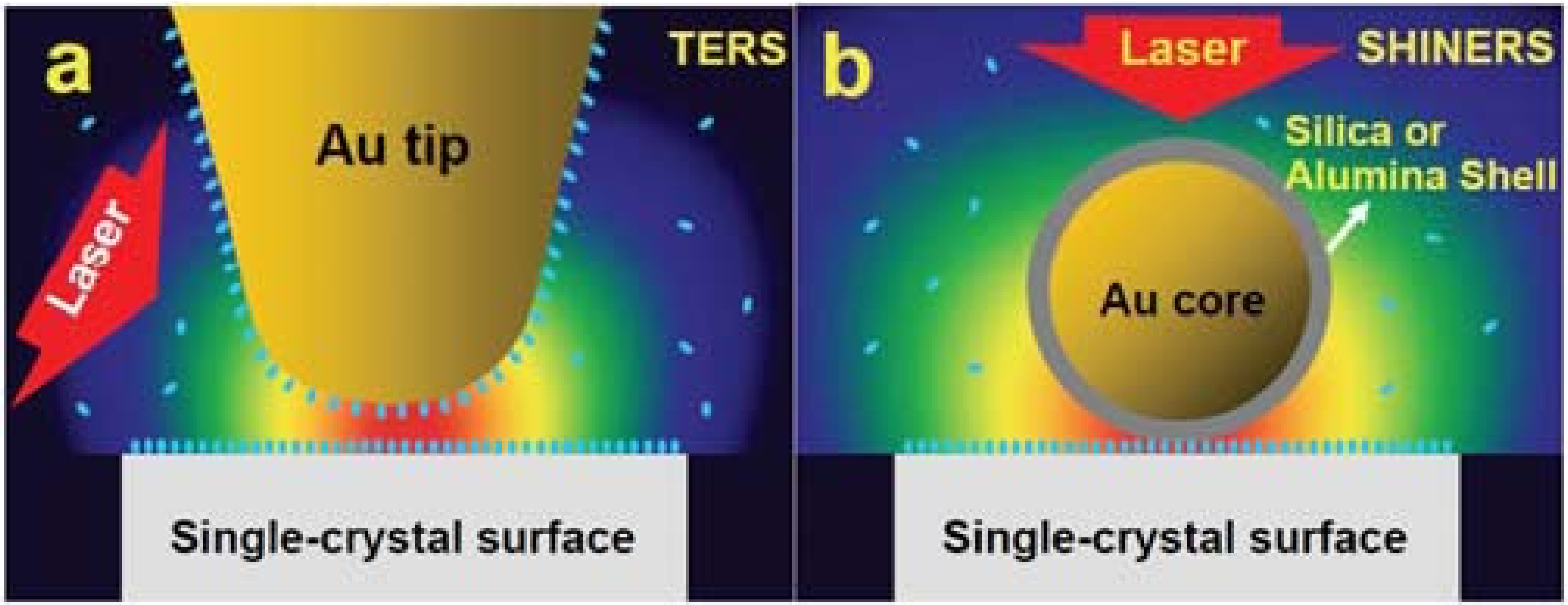
The 3D-FDTD simulation of the optical electric field distribution of a 2 × 2 array of 55 nm Au@4 nm SiO_2 NPs placed on a single-crystal gold surface. **a,** Side view and **b,** Top-view of the electric field distribution at the gap between the particle and the surface. The shell-to-shell distance is 4 nm. The polarization of the 632.8 nm laser is indicated in **b**.

Shell thickness dependent Raman signal

The electric field enhancement is considerably higher for the thinner shell



a, SHINERS spectra of pyridine (Py) adsorbed on a smooth Au surface coated with 55 nm Au@SiO_2 NPs with different silica shell thickness. **b,** The shell thickness dependence of the integrated SHINERS intensity of Py (black square) and the corresponding 3D-FDTD calculation result (red triangle). The FDTD simulation of 2 × 2 array of Au@SiO_2 with different shell thickness: **c,** 2 nm and **d,** 8 nm.


a
TERS
Au tip
Laser
Single-crystal surface
b
Laser
SHINERS
Silica or
Alumina Shell
Au core
Single-crystal surface

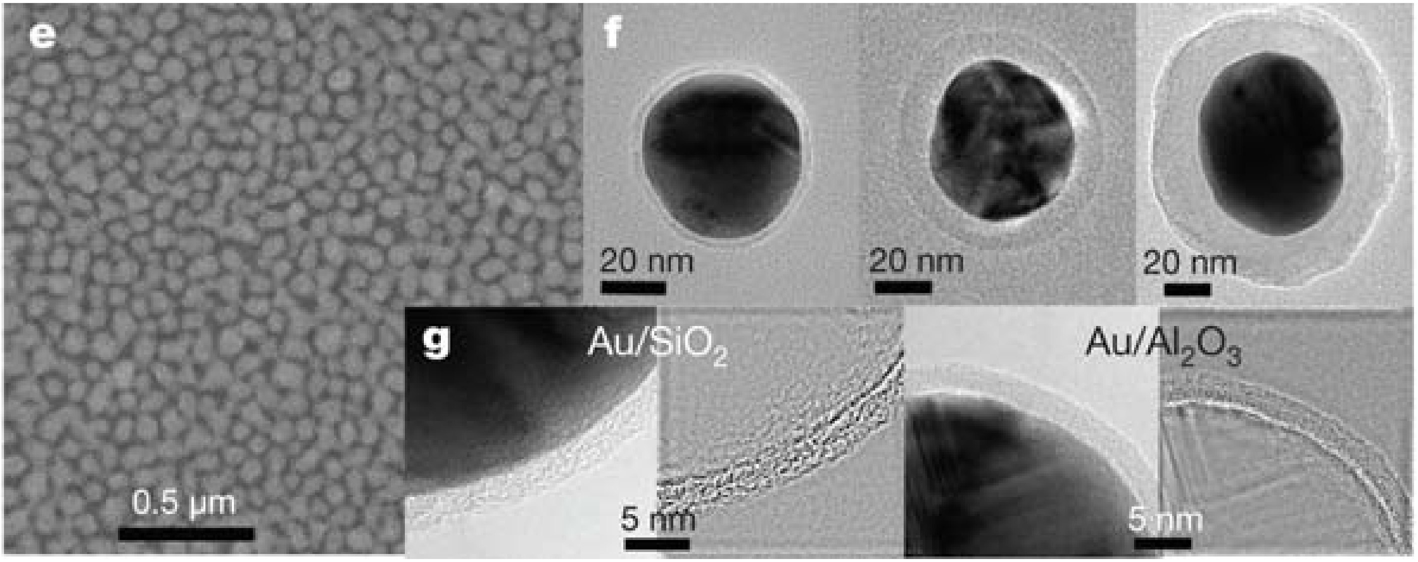
Experimental

Preparation of Au@SiO_2 core-shell NPs

A freshly prepared aqueous solution of 1 mM (3-Aminopropyl) trimethoxysilane (APS) was added to the Au@Citrate sol under vigorous magnetic stirring in 15 min. Then a 0.54 wt% sodium silicate solution was added to the sol, again under vigorous magnetic stirring. Temperature was maintained at 90 ^{0}C.

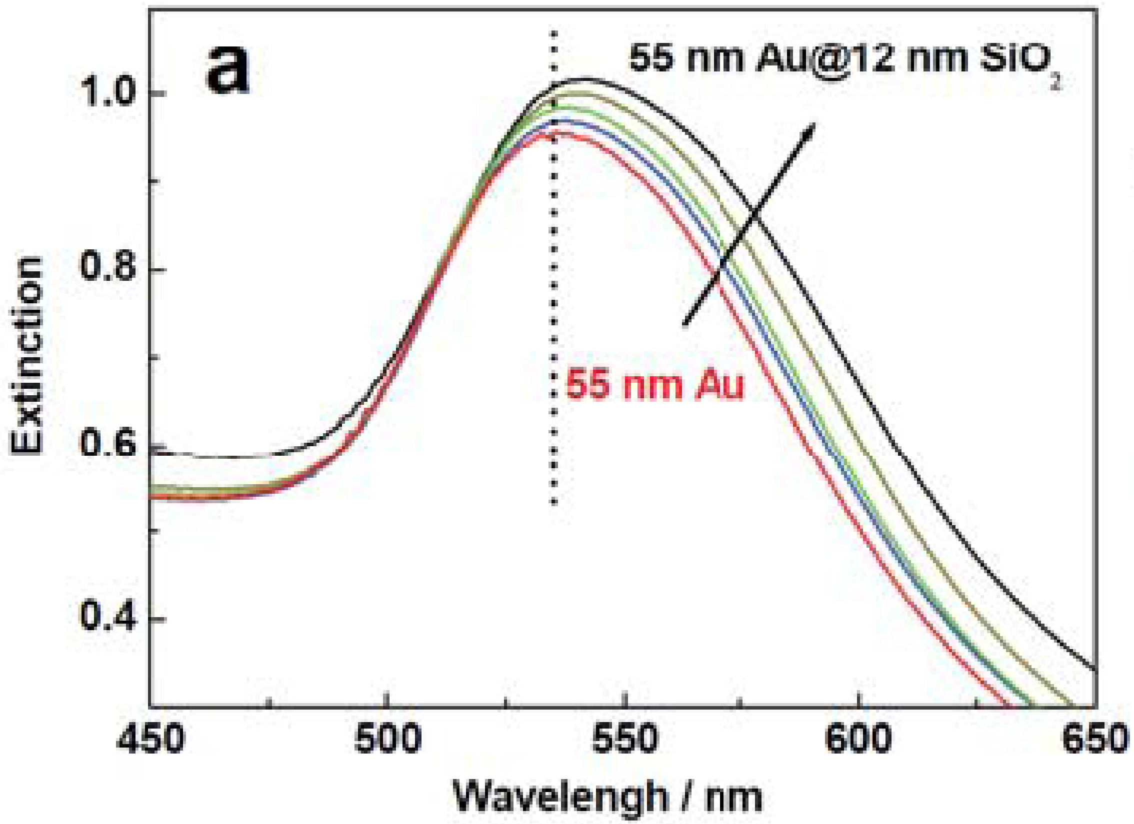
Preparation of Au@Al_2O_3 core-shell NPs

The Au@Al_2O_3 core-shell NPs were prepared by atomic layer deposition (ALD) technique.



e, Scanning electron microscope image of a monolayer of Au/SiO_2 nanoparticles on a smooth Au surface. f, HRTEM images of Au/SiO_2 core–shell nanoparticles with different shell thicknesses. g, HRTEM images of Au/SiO_2 nanoparticle and Au/Al_2O_3 nanoparticle with a continuous and completely packed shell about 2 nm thick.

The experimental extinction spectra



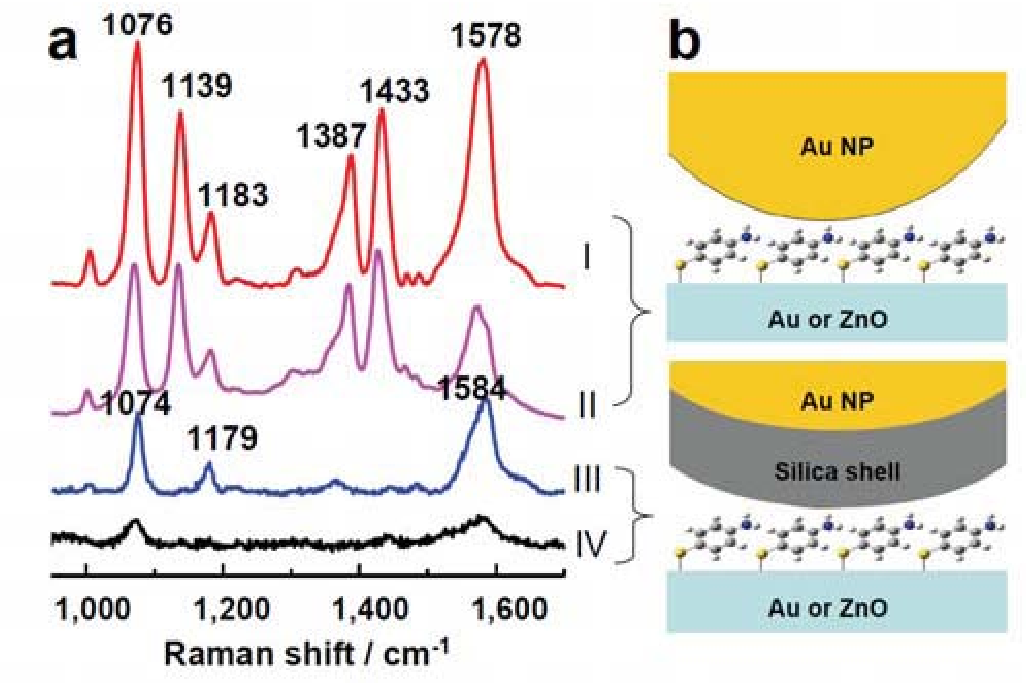
Extinction spectra of 55 nm Au@SiO_2 NPs with different silica shell thicknesses from about 1 nm, 2 nm, 4 nm up to 12 nm in comparison with that of bare 55 nm Au NPs.

Advantages of SHINERS

❖ **For studying the self-assembled monolayer system effectively**

➢ No direct contact between functional groups and Au NPs.

➢ No change in the electron density distribution in the molecule and its adsorption behavior as well as SERS features.



Photocatalytic dimerization of PATP into an aromatic azo compound takes place in presence of bare Au NPs .

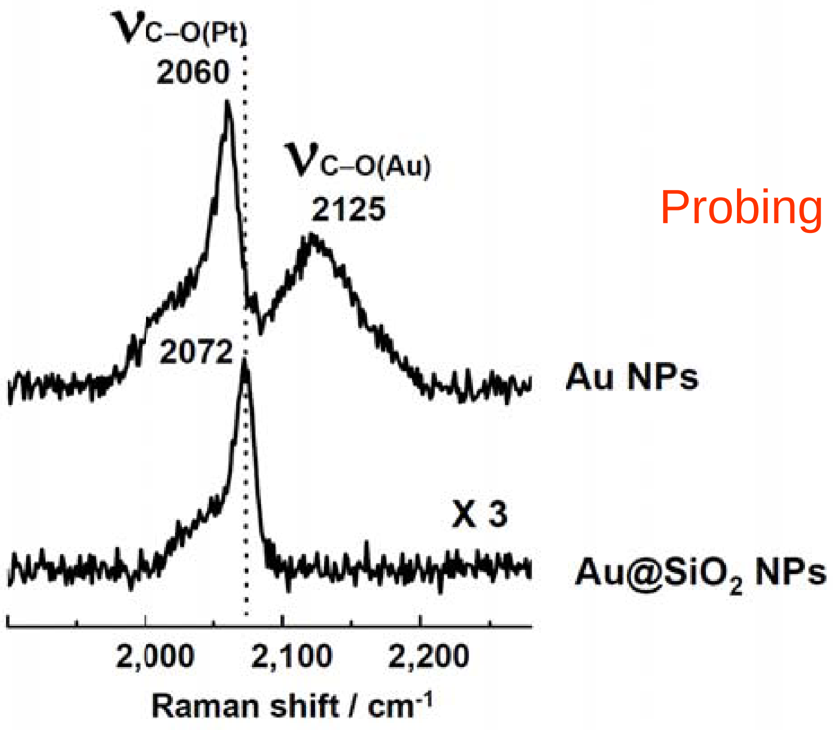
PATP = p-aminothiophenol

a, SERS or SHINERS spectra of PATP molecules interconnected in different sandwich configurations: (I) Au/PATP/Au NPs, (II) ZnO/PATP/Au NPs, (III) Au/PATP/Au@SiO_2 NPs and (IV) ZnO/PATP/Au@SiO_2 NPs.; **b,** Schematic illustration of the two different sandwich configurations.

Advantages of SHINERS

❖ **The electric contact.**

- There is no charge transfer.
- No change in molecular electronic structure.
- No photo-catalysis reaction.



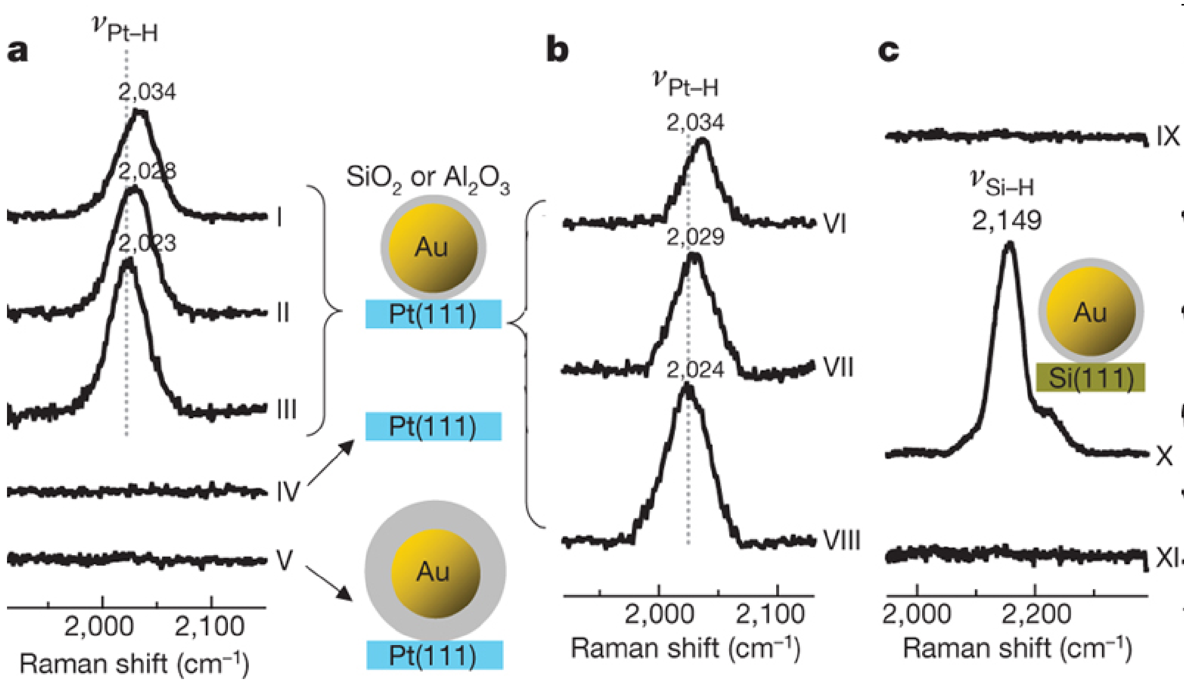
Probing CO adsorbed on a single crystal Pt(111) surface

SERS and SHINERS spectra of CO adsorbed on a Pt(111) electrode surface, recorded by Au NPs (up) or Au@SiO_2 NPs (low) in a solution of 0.1 M $HClO_4$ saturated by CO gas.

Application of SHINERS

❖ Detection of hydrogen adsorption on single-crystal flat surfaces of Pt and Si by SHINERS.

➢ No Raman spectrum of any hydrogen adsorbed at single-crystal surfaces has been reported because of its extremely low Raman cross-section.

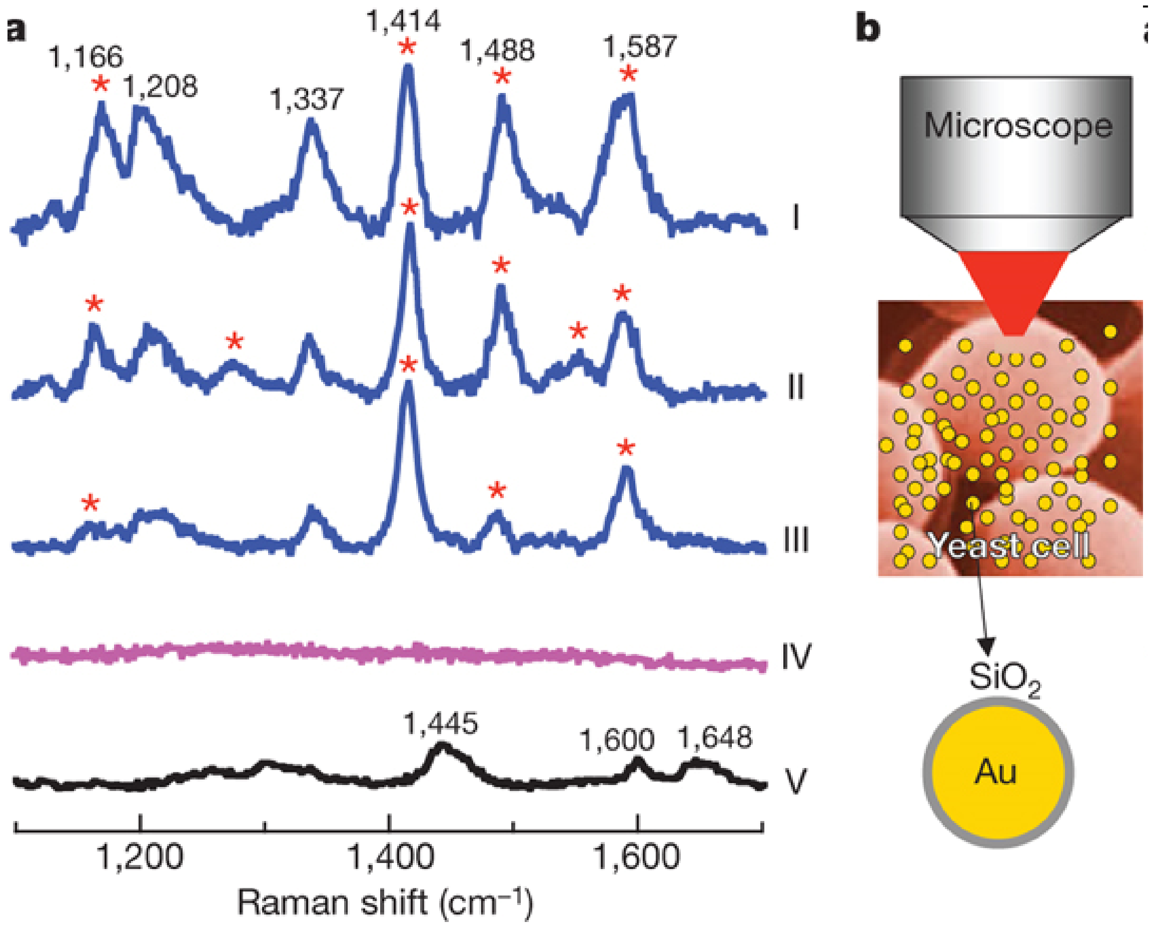


SHINERS has a potential application in semiconductor industrial processes.

a, Potential-dependent SHINERS spectra of hydrogen adsorbed on a Pt(111) surface. Curve I, at 21.2 V; curve II, 21.6 V; curve III,21.9 V; curve IV, without Au/SiO_2 nanoparticles; curve V, with the thicker shell nanoparticles at 21.9 V. b, Same study using Au/ Al_2O_3 nanoparticles. SHINERS spectra on Si(111) wafer treated with 98% sulphuric acid (curve IX), 30% HF solution (curve X) and O_2 plasma (curve XI).

Application of SHINERS

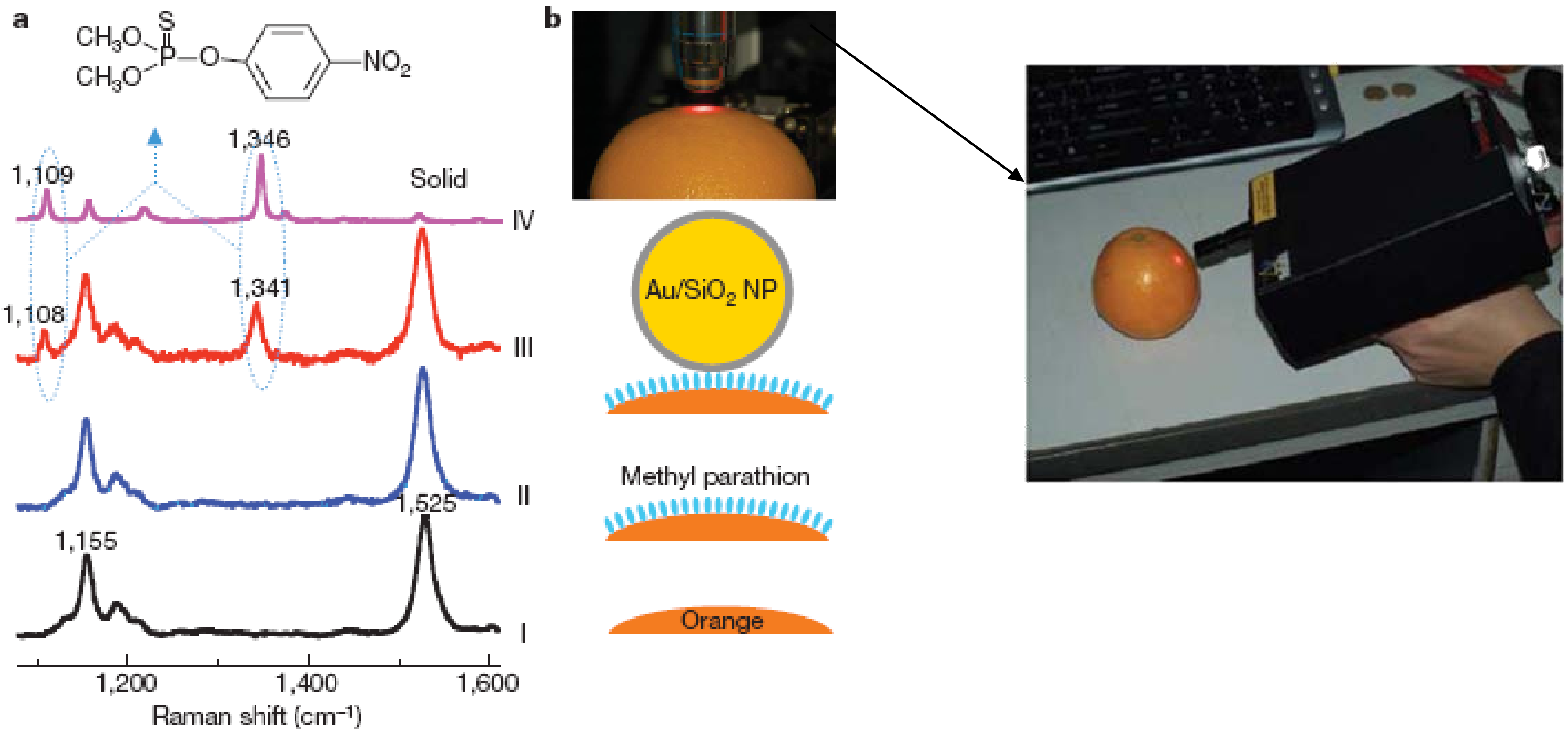
In biology: In situ probing of biological structures by SHINERS



a, Curves I, II and III, SHINERS spectra obtained from the wall of an yeast cell incubated with Au/SiO_2 nanoparticles. Curve IV, the spectrum recorded from a substrate coated with Au/SiO_2 but without a yeast cell; curve V, a normal Raman spectrum for yeast cells. The peaks marked with red asterisks are closely related to mannoprotein. b, Schematic of a SHINERS experiment on living yeast cells.

Application of SHINERS

Inspection of pesticide residues on fruits with portable Raman spectrometer



a, Normal Raman spectra on fresh citrus fruits. Curve I, with clean pericarps; curve II, contaminated by parathion. Curve III, SHINERS spectrum of contaminated orange modified by Au/SiO_2 nanoparticles. Curve IV, Raman spectrum of solid methyl parathion. Laser power on the sample was 0.5mW, and the collected times were 30 s. b, Schematic of the SHINERS experiment.

Conclusions

- An approach named as shell-isolated nanoparticle-enhanced Raman spectroscopy, in which the Raman signal amplification is provided by gold nanoparticles with an ultrathin silica or alumina shell has been demonstrated.
- This method significantly expands the flexibility of SERS for useful applications in the materials and life sciences, as well as for the inspection of food safety, drugs, explosives and environment pollutants.
- The concept of shell-isolated-nanoparticle enhancement may also be applicable to more general spectroscopy such as infrared spectroscopy, sum frequency generation and fluorescence.
- The main virtue of such a shell-isolated mode is its much higher detection sensitivity and vast practical applications to various materials with diverse morphologies.
- SHINERS will be developed into a simple, fast, non-destructive, flexible and portable characterization tool widely used in basic and applied research in the natural sciences, industry and even daily life.

Thanks