

RAMAN SPECTROSCOPY

Tipping point

Tip-enhanced Raman spectroscopy can be used to characterize the relationship between the topography and the chemical activity of individual surface sites.

Guillaume Goubert and Richard P. Van Duyne

Advances in heterogeneous catalysis must rely on the rational design of new catalysts. This requires the ability to characterize the relationship between topography and chemical reactivity at the single site level. Measurements should be designed to extract the molecular structure and the adsorption geometry at the same time. Transmission electron microscopy and scanning probe microscopy deliver the required spatial resolution; but fall short on chemical information content. On the other hand, vibrational spectroscopy provides detailed information on the structure and identity of adsorbates; but is usually limited in resolution by the diffraction of light. Writing in *Nature Nanotechnology*, Bin Ren and co-workers from Xiamen University and the University of South Carolina now present a study of surface sites using tip-enhanced Raman spectroscopy (TERS) in which they have demonstrated a spatial resolution of 3 nm paired with the chemical information content of Raman spectroscopy¹.

TERS is a member of a family of techniques designed to overcome the optical diffraction limit by using the local electromagnetic field concentrated at a sharp tip (near-field)². Among these techniques, TERS has demonstrated the highest resolution, with recent reports reaching sub-nanometre levels³ and the ability to discriminate between neighbouring surface phases or molecules^{4–6}. In TERS, a sharp tip, made of a plasmonic metal (usually Au or Ag) is scanned over a surface with sub-nanometre precision using a scanning probe setup. The volume between the probe and the surface contains an intense electromagnetic field (hot spot), which maps the Raman response under the tip apex during scanning (Fig. 1a,b).

Ren and co-workers prepared a well-defined surface consisting of a submonolayer coverage of Pd on top of a Au(111) surface. They studied the chemisorption of phenyl isocyanide (PIC) on Au and Pd terraces versus step sites. TER spectra show clear differences between Au and Pd domains due to the differences in surface coverage and

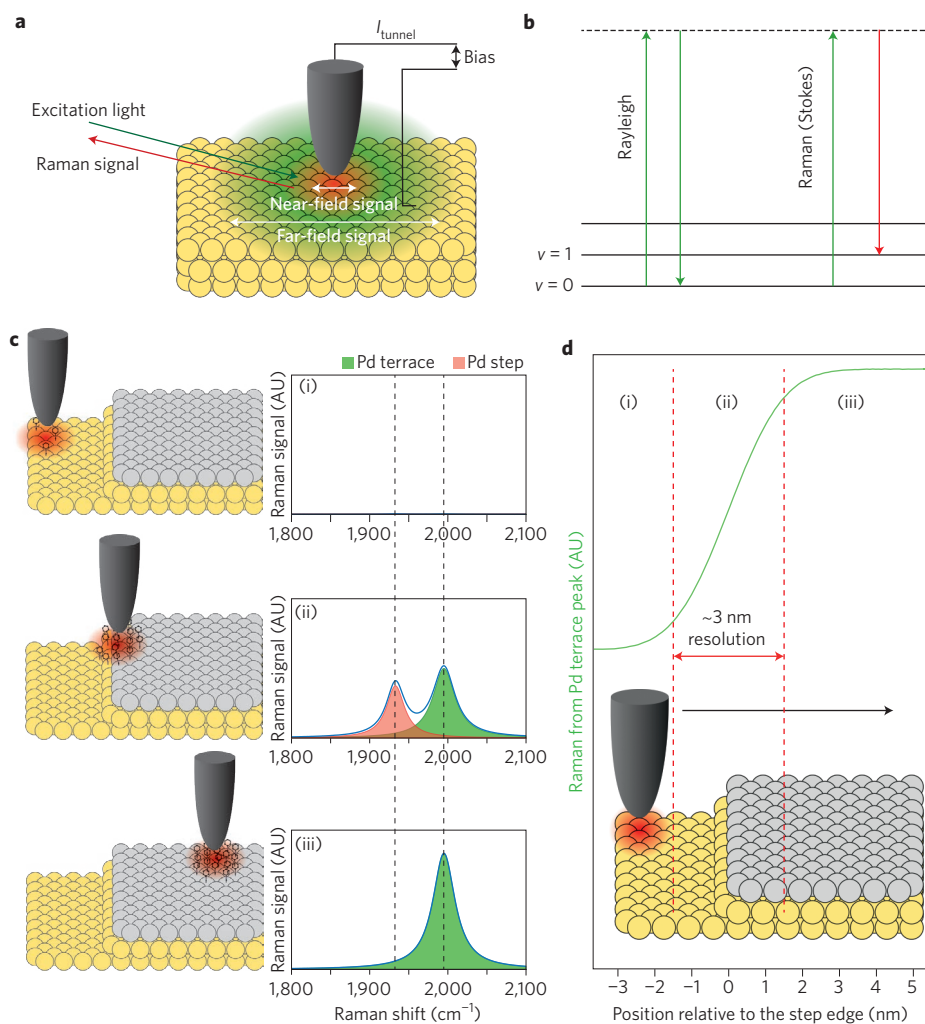


Figure 1 | Nanoscale resolution at a Pd/Au interface using Raman spectroscopy. **a**, Experimental setup for TERS using a scanning tunnelling microscope. The signal comes from a very small volume under the tip apex. **b**, Energy diagram for Raman scattering showing the wavelength-shifted Stokes signal. **c**, Raman spectra can reveal bands related to different surface sites originating from different adsorption geometries. **d**, TERS can be acquired at different points over the surface to provide nanoscale resolution with a rich chemical content.

chemisorption properties of PIC on the two different metal surfaces. The researchers also acquired TER spectra across Pd/Au atomic steps. The TERS line scans show that a peak characteristic of the C≡N moiety of the PIC molecules, which is directly bound

to surface atoms, is redshifted by 60 cm⁻¹ at the Pd edge compared with the Pd terrace (Fig. 1c). This is consistent with DFT calculations that show that the degree of back donation from the *d* band of the metal to the antibonding π* orbital of PIC at the

step site is greater than at the terrace sites. This back donation weakens the C≡N bond which should make PIC more reactive on Pd steps than on Pd terraces.

But more importantly, Ren and co-workers have demonstrated that vibrational spectroscopy can be used to study well-defined surface features at the atomic level. Until now, TERS mapping of reaction sites (with resolutions only as high as 10 nm) has been limited to ill-defined surfaces where no structure–activity relationships could be derived⁷. Interestingly, Ren and co-workers observe an increased TERS signal at the step edge, possibly due to an increased field concentration at sharp metallic features (lightning rod effect). This means that TERS can be specifically sensitive to sharp features on a catalytic surface such as steps, kinks, isolated adatoms or metal/oxide interfaces, which are thought to be the active sites in a variety of reactions.

However, in order to be more readily applicable to the analysis of catalytic systems at the nanoscale, TERS needs to demonstrate its generality with respect to substrates and adsorbates. For instance, TERS is being used very successfully on Au or Ag, because it takes advantage of the hybridization between the plasmon

resonances of the tip and sample (gap plasmon). This is expected to result in roughly a factor of 10 enhancement compared with other metals⁸; high resolution mapping of 10 nm or less has yet to be demonstrated on non-plasmonic substrates. More importantly, TERS needs to be demonstrated for technologically relevant reactions that often involve small molecules such as CO or short chain hydrocarbons. This is challenging since the Raman cross-sections for few-atom adsorbates can be 2–3 orders of magnitude less than large aromatic molecules. TERS of adsorbed molecules that do not possess an electronic resonance at the laser excitation wavelength show an electromagnetic enhancement of only 4–6 orders of magnitude with respect to the same molecule in solution. This is sufficient to observe a few hundred molecules under the tip at packing densities near full monolayer coverage; but to achieve single molecule sensitivity, an additional resonance enhancement of 3–6 orders of magnitude is required⁹. One route to the generalization of TERS would be to develop it in the UV, where many organic molecules are resonant. Additionally, the production of stable and strongly enhancing tips with high yield

is critical to lower the entry barrier into the field and increase the number of users both for basic science and technological purposes. If current trends continue and TERS can be demonstrated under a wider range of experimental conditions, including realistic *in situ* studies, it is destined to become a major analytical technique for heterogeneous catalysis, given its large chemical information content. □

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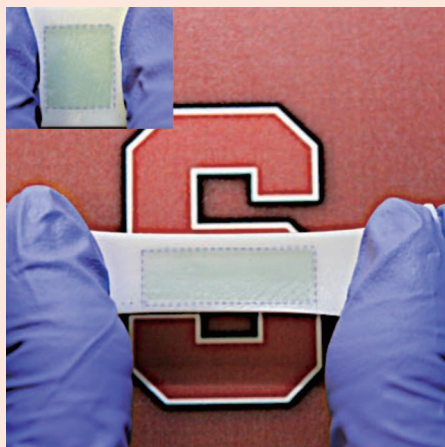
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WEARABLE ELECTRONICS

Stretching the limits

Wearable electronic devices are designed to maintain their functionality throughout multiple bending cycles. Because they require structural flexibility, such devices have to be fabricated from plastic-like materials that are far less rigid than conventional high-mobility semiconductors. However, in softer semiconductors such as π -conjugated polymers achieving the desired level of stretchability in combination with good charge transport properties remains elusive. High-mobility polymers with rigid chains and improved crystallinity tend to be brittle, while their amorphous and mechanically flexible counterparts have low electrical conductivity. Jie Xu, Sihong Wang *et al.* have now shown how this mutual exclusivity of mechanical and electrical performance can potentially be overcome via nanoconfinement (*Science* **355**, 4496; 2017).

Constraining polymer chains into nanosized dimensions is known to modify their kinetic and thermodynamic properties. If successfully executed,



this approach may result in the improved ductility and suppressed crystallinity of the confined polymer. The so-called CONPHINE methodology inspired by the idea of nanoconfinement was applied to fabricate a hybrid material made of conducting DPPT-TT nanofibrils embedded

into SEBS, a highly deformable elastomer. Increased chain dynamics and reduced crystallization were observed in the thinnest polymer/SEBS films. The aggregates of the conducting polymer remain perfectly interconnected and good charge transport is maintained throughout the nanoscale network. The picture shows a flexible transistor fabricated from the DPPT-TT/SEBS stretched to twice its length. Only minimal loss in mobility and on current is observed in this experiment. During the strain test conducted on a SEBS substrate, conducting channels showed no visible cracking even when investigated at the nanoscale. The stretchable thin film transistors were able to sustain their performance after more than 1,000 repeated stretching cycles. The method was proven equally successful when tested on other conducting polymers, with one of them exhibiting mobility of $1 \text{ cm}^2 \text{ Vs}^{-1}$ at 100% strain.

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