#### SPECTROSCOPY

## Sub-molecular photoluminescence

Photoluminescence spectroscopy using atomic-scale light reveals an optical transition of a single molecule at sub-nanometre resolution.

### Takashi Kumagai

ealizing optical spectroscopy at atomic resolution is one of the ultimate goals of nano-optics. Precise engineering of plasmonic nanostructures allows confining light to nanoscopic volumes and even down to the atomic scale<sup>1</sup>. Nanoscale optical imaging using plasmonic fields has been explored in scanning near-field optical microscopy over the past three decades. However, sub-nanometre-resolution imaging has proven to be elusive and it is only very recently that scientists have made atomic-scale light available for optical spectroscopy. This has been successfully demonstrated by the angström-level resolution in low-temperature tip-enhanced Raman spectroscopy of a single molecule anchored on a metal surface, enabling the visualization of individual vibration modes in real space<sup>2,3</sup>.

The exceptionally high sensitivity and spatial resolution originate from the extreme enhancement and confinement of a plasmonic field in a sub-nanometre gap, a so-called picocavity<sup>4</sup>. The use of a low-temperature scanning tunnelling microscope (STM) allows the control of such a tiny gap in three dimensions with sub-nanometre precision. As shown in Fig. 1, the highly localized and intense plasmonic field can be created at an atomistic protrusion on a plasmonic tip. Propagating light (far field) resonantly couples with the tip base with a typical diameter of a few hundreds of nanometres and generates confined light (near field), which is further concentrated at the atomistic protrusion through the non-resonant, atomic-scale lightning rod effect5. Because of its extreme confinement, the resulting atomic-scale light is accessible only at a very short gap distance, below ~1 nm (Fig. 1c).

Now, writing in *Nature Photonics*, Ben Yang and colleagues report another milestone in atomic-scale optical spectroscopy, that is, tip-enhanced photoluminescence of single molecules with a spatial resolution down to ~0.8 nm (ref. <sup>6</sup>). This remarkable demonstration is attained by overcoming several technical challenges.



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**Fig. 1** | **Generation of atomic-scale light at an atomistic protrusion on a plasmonic tip. a**, Model of the STM junction for simulation. **b**, Atomistic protrusion on the apex of the tip. **c**, Simulated field enhancement in the STM junction. The enhancement on the surface at different gap distances,  $d_{gap}$ , is plotted. The solid (dashed) lines correspond to the field enhancement with (without) the atomistic protrusion. The inset shows the distribution of the field enhancement in the junction. Figure reproduced with permission from ref. <sup>12</sup>, American Chemical Society.

Figure 2 illustrates the experiment conceived by Yang and colleagues, consisting of a plasmonic silver tip and a single zinc phthalocyanine molecule isolated on an ultrathin sodium chloride film on a silver surface. The measurement principle is the same as for conventional scattering-type scanning near-field optical microscopy. The junction is illuminated by a narrowband, continuous-wave laser at 532 nm, generating a strong plasmonic field interacting with the molecule, and the resulting molecule-specific emission band around 653 nm is detected. The plasmonic junction acts as a highly efficient optical antenna to enhance the molecular excitation and emission. whereby the enhancement factor of the photoluminescence reaches the order of ~10<sup>8</sup>, yielding the single-molecule sensitivity.

As already mentioned, the extreme confinement of plasmonic fields arises from the atomistic structure in the sub-nanometre plasmonic gap<sup>7</sup>. Yang and colleagues demonstrate tip-apex engineering using single-atom manipulation and the apex is constructed by picking up individual silver atoms. Although the silver surface is necessary to generate the strong gap-mode plasmon, fluorescence quenching occurs when the molecule is directly attached to a metal through non-radiative damping of the excited state<sup>8</sup>. The ultrathin sodium chloride film is introduced to electronically decouple the zinc phthalocyanine molecule from the silver surface while keeping sufficient field enhancement in the junction. The delicate balance between field enhancement and fluorescence quenching is regulated by the

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**Fig. 2** | **Tip-enhanced photoluminescence spectroscopy of a single zinc phthalocyanine molecule. a**, Schematic of the experimental set-up. *V*<sub>bias</sub>, bias voltage. **b**, STM image of the molecule. **c**, Photoluminescence (PL) image, revealing sub-molecular resolution. Figure adapted with permission from ref. <sup>6</sup>, Springer Nature Ltd.

thickness of the sodium chloride film — a three-monolayer thickness is adopted to yield the best compromise. In addition, fluorescence quenching is examined by moving the silver tip towards the molecule. Interestingly, the researchers find that the photoluminescence becomes even stronger at a vanishing distance between the tip and the molecule and that quenching finally occurs when the tip is in contact with the molecule. This observation suggests that the rate of the molecular excitation and light emission enhanced by the atomic-scale plasmonic antenna is significantly larger than the non-radiative damping of the excited state into the metal unless the molecule is electrically fused with the silver tip.

Tip-enhanced photoluminescence with atomic-scale light is fundamentally different from conventional single-molecule spectroscopy with far-field optics in terms of light-molecule (exciton) interactions. Because the spatial extent of propagating light (hundreds of nanometres) is much larger than the size of the molecule (about 1 nm), the interaction can be well understood by the long-wave approximation in which the spatial variation (inhomogeneity) of the electromagnetic field is neglected and the molecule is treated as a point dipole. This approximation is commonly employed to describe lightmatter interactions. However, when the plasmonic field is confined to the atomic scale, it becomes essential to consider the spatial variation of both the electromagnetic field and chemical structure in order to determine the molecular electronic transitions, leading to the failure of the point-dipole approximation and to the

change in the optical selection rules. This effect in plasmon–exciton coupling, for instance, has been observed in scanning tunnelling luminescence spectroscopy<sup>9–11</sup>. Now, as demonstrated by Yang and colleagues, sub-molecular-resolution photoluminescence imaging of the zinc phthalocyanine molecule clearly resolves the four lobes in the light-emission pattern (Fig. 2c), reflecting the molecular electronic transition. Such an anisotropic feature associated with the chemical structure cannot be described when the molecule is treated as a point dipole.

Tip-enhanced photoluminescence is also fundamentally different from well-established scanning tunnelling luminescence. In the latter case, the gap-mode plasmon is excited by highly localized tunnelling electrons via inelastic processes. Therefore, the molecular luminescence essentially involves electron-molecule interactions, which may complicate the photophysical processes. In addition, the relatively high bias voltage applied to launch the gap-mode plasmon (typically more than 2 V) makes the molecular junction unstable. Optically excited tip-enhanced photoluminescence demonstrated by Yang and colleagues is free from these problems and offers a new opportunity to elucidate subtle plasmonmolecule interactions. The interaction between the molecular exciton and the adjacent plasmonic nanoantenna causes 'self-interaction' through a back-action of the radiated field, which affects the Purcell factor and the Lamb shift that are relevant to the enhancement and energy shift, respectively, of molecular spontaneous emission. The peak position mapping of the tip-enhanced photoluminescence clearly resolves the Lamb shift within the single zinc phthalocyanine molecule<sup>6</sup>. In addition, the Purcell factor is discussed with respect to the variation in the peak linewidth. These results highlight the importance of simultaneously considering the spatial distribution (inhomogeneity) of the plasmonic field and the molecular electronic states in order to accurately describe photoluminescence with atomic-scale light.

The sub-nanometre resolution depends crucially on the stability of the atomistic protrusion on the apex of the plasmon-active tip, thus requiring low temperatures. At elevated temperatures, the spatial resolution suffers from the thermal fluctuations of the atomistic structure on the apex, which hampers the reliable manipulation of atomic-scale light. This will be the fundamental technical challenge to overcome in the future to realize ultra-high sensitivity and resolution under ambient conditions and in solutions. Another technical challenge is the requirement of a strong gap-mode plasmon, which imposes a limitation on the choice of the sample that can be measured. Nevertheless, the demonstrated experimental approach by Yang and colleagues will create great opportunities for studying intriguing atomic-scale light-molecule interactions with unprecedented precision. In addition to tip-enhanced Raman and scanning tunnelling luminescence, tip-enhanced photoluminescence will revolutionize the capabilities of the low-temperature scanning probe microscope.

The simultaneous use of established techniques, such as single-atom/molecule manipulation, inelastic electron tunnelling spectroscopy and ultra-high-resolution atomic force microscopy with atomic-scale optical spectroscopy, may provide versatile approaches to investigate many important phenomena in nanoscale physics and chemistry. In particular, tip-enhanced optical spectroscopy may pave the way for time-resolved experiments in combination with ultrafast pulsed lasers. This may lead to optical spectroscopy at the intrinsic space and time scales of electron and nuclear dynamics, which will open a new frontier of observing single-molecule chemistry in real space and real time. 

#### Takashi Kumagai <sup>[]</sup>,2 <sup>[]</sup>

<sup>1</sup>Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany. <sup>2</sup>Institute for Molecular Science, Okazaki, Japan. <sup>™</sup>e-mail: kuma@fhi-berlin.mpg.de

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#### **Competing interests**

The author declares no competing interests.

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# A free-electron laboratory coherent X-ray source

Facilities generating coherent X-rays tend to be large scale and costly. Now researchers have demonstrated a parametric and coherent laboratory-scale X-ray source by passing moderately energetic electrons through van der Waals heterostructures.

#### Ingo Uschmann

ince the first use of synchrotron radiation in the X-ray range, much development of storage rings combined with insertion devices based on periodical magnetic structures, especially undulators, has now enabled brilliant X-ray sources, for example, facilities based on diffraction-limited storage rings or X-ray free-electron lasers. Stored electrons can possess highly relativistic energies of a few gigaelectronvolts (Fig. 1) and the only electron energy loss is related to the emission of electromagnetic radiation when the electrons are accelerated. Owing to the highly relativistic energy, the X-ray emission direction, which is like a dipole in the rest frame, is collimated in the laboratory frame on the order of a few microradians. This divergence is smaller than for most conventional lasers in the visible range. The emitted photon energy range of an undulator is typically a few tens of kiloelectronvolts and can be easily tuned by the gap of the undulator as well as by varying the electron energy.

The number of such X-ray research facilities is growing all over the world, and chemists, biologists, physicists, archaeologists and art scientists perform research using specialized experimental stations located around the storage ring. Nevertheless, the brilliant radiation is rare and costly.

Now, writing in Nature Photonics Shentcis and colleagues report that special van der Waals materials could also be used to generate parametric X-ray radiation (PXR) and coherent bremsstrahlung (CBS) with relatively low electron energies between 60 keV and 300 keV, which were produced by a transmission electron microscope<sup>1</sup>.



Fig. 1 | Scaling of the electron velocity,  $v_{\text{electron}}$  and the relativistic parameter,  $\gamma$ , for different X-ray sources. For laboratory X-ray sources (tubes) non-relativistic electrons are used in contrast to modern synchrotron radiation facilities where strongly relativistic electrons are used. In their work, Shentcis and colleagues used medium relativistic electrons to induce PXR and CBS inside van der Waals materials.  $E_{\text{photon}}$  is the X-ray photon energy and c is the speed of light.

PXR and CBS are excited when an accelerated charged particle travels inside crystalline matter and were first considered by von Weizsäcker and by Williams in 1934 (refs. <sup>2,3</sup>). An approach for realizing a laboratory-scale coherent X-ray source was proposed by Überall in 1956 (ref. 4), who published results on relativistic electrons

passing through a perfect crystal. In that case, the wavelengths of the electrons are shorter than the lattice spacing of the crystal. Owing to the periodic interaction of the electron with the crystal lattice, interference of the produced CBS can occur in certain directions predetermined by the atomic planes<sup>5</sup>. In contrast, if the particle