Supporting Information;

Near-Field Spectral Response of Optically Excited Scanning Tunneling Microscope Junctions Probed by Single-Molecule Action Spectroscopy

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1. Analysis of peak sharpness in the near-field action spectra

It appears that the sharpness of the multiple peaks in the action spectra is different between the non-FIB tip (**Fig. 3**) and the grooved FIB-tip (**Fig. 6b**). In order to quantify the difference, we analyzed differential near-field action spectra ($\Delta\sigma/\Delta E_{\mathrm{in}}$) for the data in **Figs. 3**, **5e**, and **6b**. **Figures S1a** and **S1b** show differential spectra and the histogram (distribution of $\Delta\sigma/\Delta E_{\mathrm{in}}$), respectively. The analysis reveals a larger dispersion (peak-to-peak amplitude) of $\Delta\sigma/\Delta E_{\mathrm{in}}$ for the multiple peaks resulting from SPPs generated by surface roughness of the tip shaft than that for the modulated peaks of the grooved tip. For 50-µm polished FIB-tip, the dispersion of $\Delta\sigma/\Delta E_{\mathrm{in}}$ in the range of the multiple peaks (<1.95 eV) is comparable with that for the non-FIB tip. This result corroborates that the multiple peaks for the FIB-tip occurs by SPPs propagating from the unprocessed part. It should be noted that the peak sharpness may be limited by the excitation laser bandwidth (6–10 nm). Therefore, the observed sharpness of the randomly modulated peaks by the SPPs represents a lower limit and it will be even sharper if the laser bandwidth was much smaller.

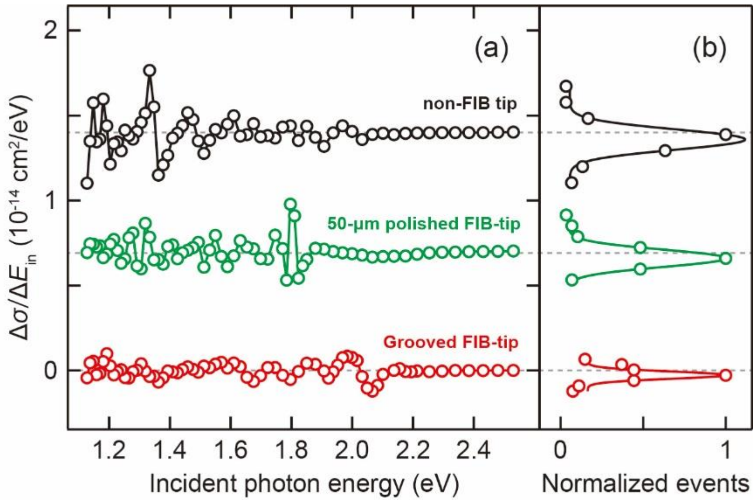

Figure S1. (a) Differential near-field action spectra ($\Delta\sigma/\Delta E_{\mathrm{in}}$) for non-FIB (black), 50-µm polished (green) and grooved FIB-tips (red). The data for non-FIB and 50-µm polished FIB-tips are vertically offset for clarity. σ: tautomerization cross section, E_{in}: Incident photon energy. (b) Histogram of $\Delta\sigma/\Delta E_{\mathrm{in}}$. The data are fitted by a Gauss function and full width at half maximum is 4.839×10^{-16}, 4.462×10^{-16} and 2.920×10^{-16} cm^2/eV for non-FIB, 50-µm polished and grooved FIB-tips, respectively.

2. Fabrication Au tips using focused ion beam milling

For the FIB milling of the Au tips we used an FEI Helios NanoLab G3 FIB-SEM DualBeam system. It provides Ga ions with an acceleration voltage up to 30 kV and enables milling and deposition of structures with critical dimensions of less than 10 nm. The Au tips were mounted on a pre-tilted specimen holder and oriented towards the ion beam such that the axis of the tip is collinear with the ion beam. We performed a multiple-step annular milling process with different parameters and a varying order, depending on the initial tip profile and the required sharpened length. Taking into account the re-deposition dynamics during ion milling and the fact, that the main re-deposition of removed material occurs underneath the ion beam incidence point at highly steep surfaces, we preferred an inner-to-outer-radius scan direction, *i.e.*, from the apex downwards, in order to simultaneously remove re-deposited material.

Several tip fabrication procedures using Focused Ion Beam (FIB) have been already suggested before.[1, 2] We introduce a similar procedure, however, with a reverse milling sequence and different parameters. We first start the tip fabrication with a low ion energy step at 5 kV in order to shape and smoothen the apex. Subsequently, we increase the inner and outer radii as well as the ion energy and beam current to obtain higher milling rates to only sharpen the shaft to the required length. This step order aims to minimize damage and Ga implantation into the apex and in close vicinity to it. Finally, we apply a low energy polishing step at 5 kV to the sharpened length of the shaft to reduce damage layer caused by 30 kV ions.

A key parameter in ion milling processes is the volume per dose value ΔV, *i.e.*, the removed material volume per primary ion. It is material-specific and determines, at a certain ion energy, the milling time t for a required depth Z and a given beam current I:

$$\Delta V = \frac{\text{Volume}}{\text{Charge}} = \frac{X\times Y\times Z}{I\times t}$$

In order to precisely control the groove depth and the milling time, we set this value to 1.5 μm^3/ nC for Au,[3] and used, at 30 kV ion energy, the lowest ion beam current of about 7 pA to avoid excessive milling and thus damaging the apex.

REFERENCES

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[1] M. J. Vasile, D. Grigg, J. E. Griffith, E. Fitzgerald, and P. E. Russell, Scanning probe tip geometry optimized for metrology by focused ion beam ion milling, Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena 9, 3569 (1991)

[2] Z.M. Wang, *FIB Nanostructures*, Lecture Notes in Nanoscale 1, Science and Technology 20, DOI 10.1007/978-3-319-02874-3, Springer International Publishing Switzerland (2013).

[3] J. Orloff, L. W. Swanson, M. Utlaut, High Resolution Focused Ion Beams: FIB and its Applications, DOI 10.1007/978-1-4615-0765-9, ©Springer Science + Business Media New York (2003).