

## Supplementary Materials for **Tip-enhanced ablation and ionization mass spectrometry for nanoscale chemical analysis**

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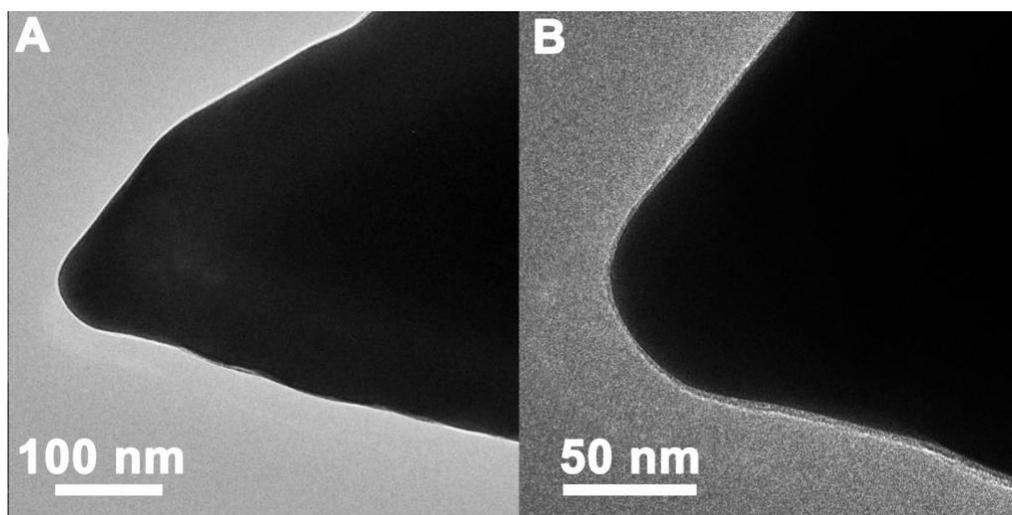
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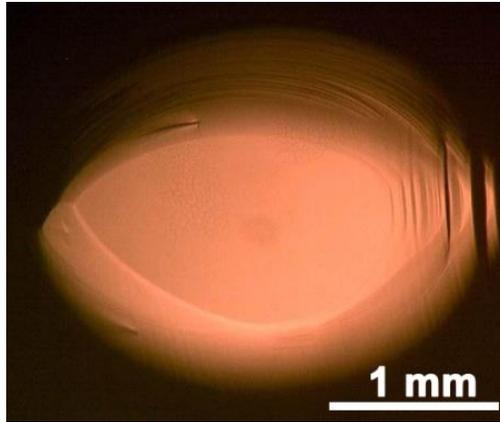
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**table S1. Operating parameters of the TEAI source.**

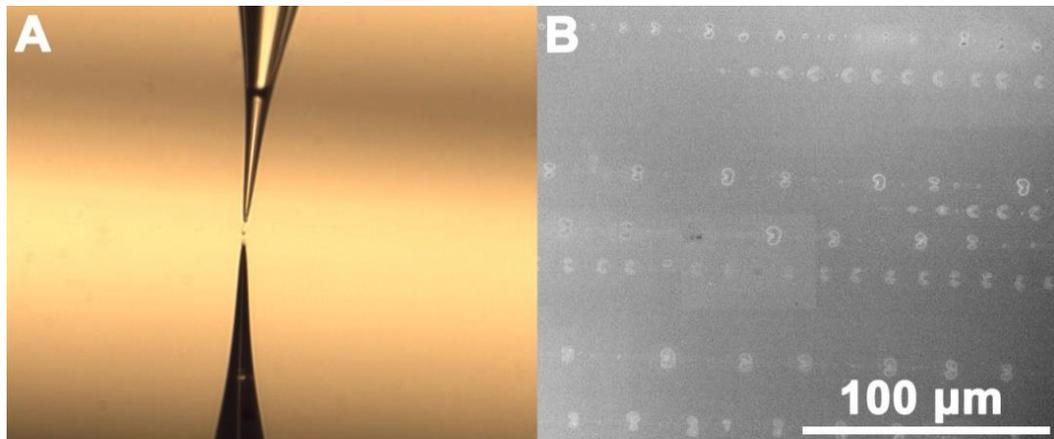
Experiment	Au @ Ti	9 salt residue	MS imaging
Laser pulse frequency (Hz)	2	2	10
Laser wavelength (nm)	515		
Laser pulse duration (fs)	500		
Polarization	p-polarization		
Laser spot ( $\mu\text{m}$ )	ellipse (400 $\times$ 565)		
Tip diameter (nm)	80		
Tunneling current (nA)	0.1	0.4	0.6
Bias voltage of STM (V)	-0.2	-0.5	-1
Operational pressure	$2.0 \times 10^{-4}$ Pa		



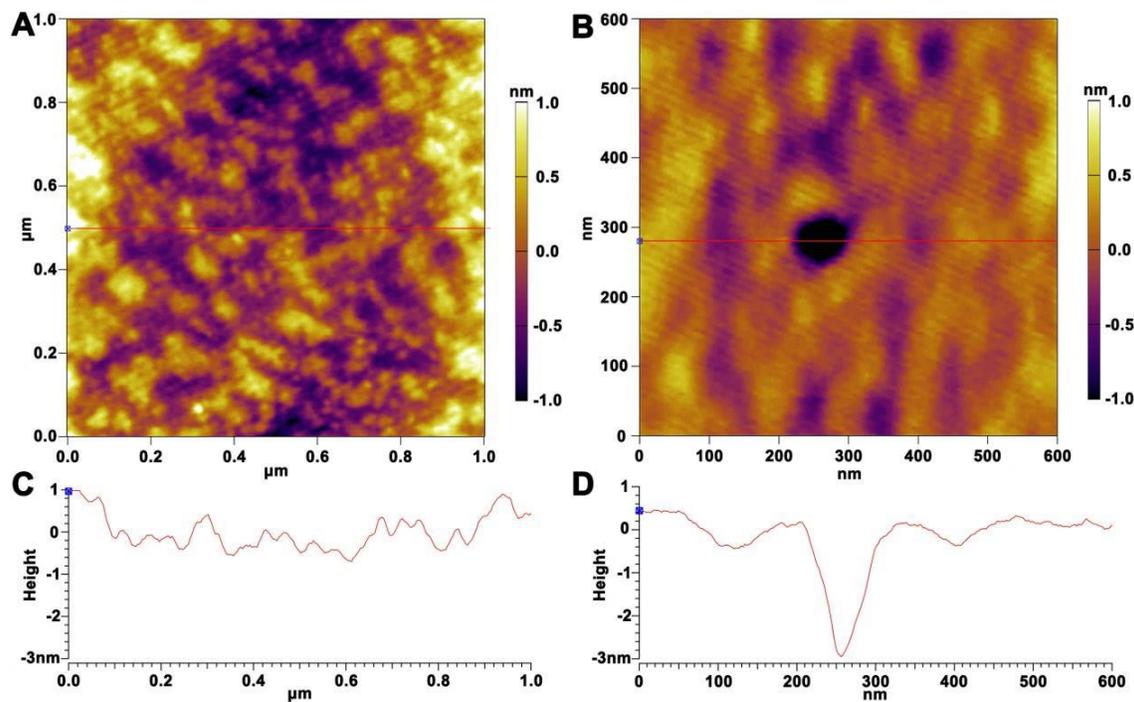
**fig. S1. Images of the shell-isolated tip.** (A) TEM image of a shell-isolated silver tip which has an apex of 80 nm in diameter, coated with a 2 nm thick layer of SiO<sub>2</sub>. (B) The enlarged TEM image of (A) shows the layer of SiO<sub>2</sub>.



**fig. S2. Picture of Au (111) with a 10-nm layer of Ti taken by a metallurgical microscope.**



**fig. S3. Preparation progress of the micropatterned KI sample. (A)** Picture of depositing droplets of KI on the single crystal silicon substrate coated with 10 nm Au on the top. **(B)** SEM image of the micro-patterned KI sample.



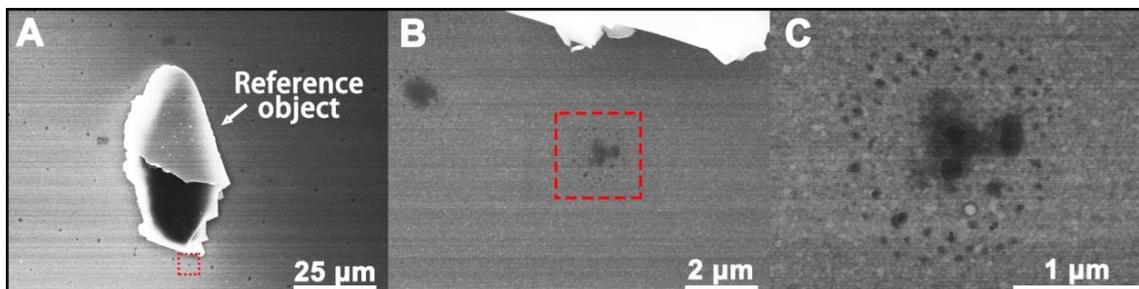
**fig. S4. AFM images of the surface of Au@Ti.** (A) AFM image of the surface of Au@Ti obtained before near-field ablation. (B) AFM image of a crater on the surface of Au@Ti obtained after tip enhanced ablation by performing 40 pulses. (C) The cross section of (A), showing the surface roughness remained within  $\pm 1$  nm. (D) The cross section of (B), showing the depth of the fs-laser induced near-field crater was approximate 3 nm.

**table S2. Experimental and theoretical ablated Ti particle numbers with 40 laser shots.**

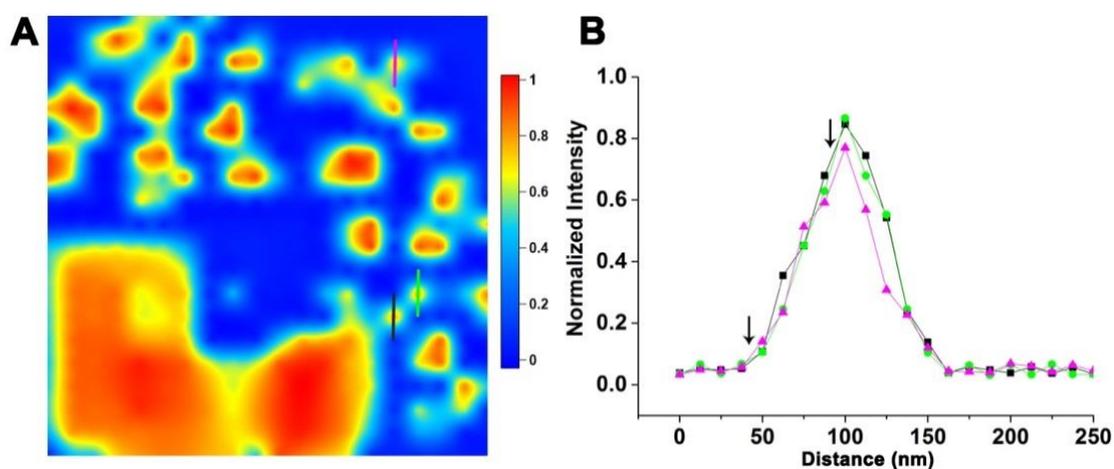
Items	Ablated atom numbers
Experimental result <sup>a</sup>	$2.22 \times 10^5$
Theoretical result <sup>b</sup>	$2.98 \times 10^5$

<sup>a</sup> calculated from the size of the crater in figs. S4B & S4D.

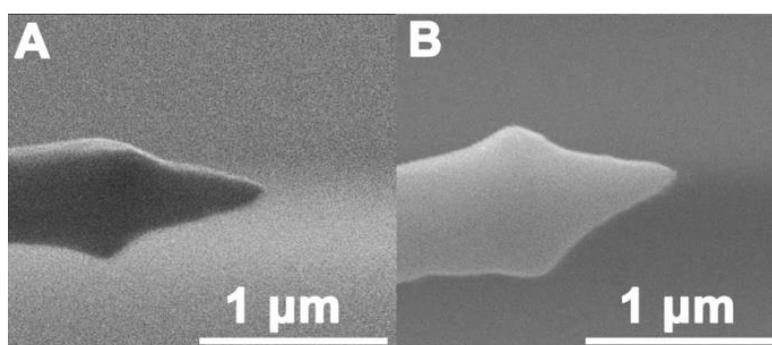
<sup>b</sup> calculated from the simulated 7472 atoms per pulse  $\times$  40 pulses.



**fig. S5. SEM images of the area of interest.** (A) SEM image of the reference object taken before MSI. The red square with red dashed line shows the residue analyzed in MSI. (B) An enlarged SEM image of the residue in (A). (C) An enlarged SEM image of the residue in (B).



**fig. S6. Demonstration of lateral resolution analysis.** (A) Image of  $^{39}\text{K}^+$  distribution obtained in fs-laser induced near-field MSI with 3 scanning lines whose sizes are  $50\text{ nm} \times 50\text{ nm}$ . (B) MS signals extracted from 3 scanning lines of (A), showing that the lateral resolution was  $\sim 50\text{ nm}$ .



**fig. S7. Morphologic comparison of tips used in TEAI experiment.** SEM images of the tip (A) before and (B) after 30000 laser shots in TEAI experiment.