Supporting Information:

Dramatic Enhancement of Tip-Enhanced Raman Scattering Mediated by Atomic Point Contact Formation

Shuyi Liu¹, Borja Cirera¹, Yang Sun², Ikutaro Hamada²,³, Melanie Müller¹, Adnan Hammud⁴, Martin Wolf¹, Takashi Kumagai¹,⁵,⁶*

¹Department of Physical Chemistry, Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

²Global Research Center for Environment and Energy based on Nanomaterials Science, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

³Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka Suita, Osaka 565-0871, Japan

⁴Department of Inorganic Chemistry, Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

⁵JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

⁶Center for Mesoscopic Sciences, Institute for Molecular Science, Okazaki 444-8585, Japan

*Corresponding author: kuma@fhi-berlin.mpg.de; kuma@ims.ac.jp
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1. **Details of experiments**

All experiments were performed in an ultra-high vacuum (UHV) chamber (base pressure $<5 \times 10^{-10}$ mbar) equipped with a low-temperature TERS (modified UNISOKU USM-1400) operated with a Nanonis SPM controller. The bias voltage ($V_{bias}$) was applied to the sample, and the tip was grounded. The tunneling current ($I_t$) was collected from the tip. The STM tips were prepared by electrochemical etching of an Ag wire and subsequently nanofabricated using focused ion beam (see Ref. 1). The tips were further cleaned by Ar$^+$ sputtering in the UHV chamber before measurement. The Ag(111) surface was cleaned by repeated cycles of Ar$^+$ sputtering and annealing up to 670 K. Ultrathin ZnO layers were grown on the clean Ag(111) surface by reactive deposition method (see Ref. 2). A bulk NaCl was evaporated from K-cell evaporator. The excitation laser is focused to the STM junction with an *in-situ* Ag-coated parabolic mirror (numerical aperture of ~0.6) mounted on the cold STM stage. In the TERS measurements, we used HeNe laser for 633 nm and solid-state lasers for 532 and 780 nm. The incident beam is linearly polarized along the tip axis (p-polarization). The scattered photons are collected by the same parabolic mirror and detected outside of the UHV chamber with a grating spectrometer (AndorShamrock 303i). The parabolic mirror was precisely aligned using piezo motors (attocube GmbH), which allow three translational and two rotational motions. The alignment was optimized by maximizing the signal of plasmon-assisted resonant electron tunneling.3
2. Correlation between the TERS intensity and the continuous background in the APC regime

We also found that the enhancement of Raman scattering in APC regime is correlated with the continuous background. Figure S1 shows the TERS spectra obtained for 2-ML ZnO at the APC. Three different tip conditions result in different features in the continuous background. When the strong background appears in the range of $\lambda_{ext}$, the TERS intensity becomes larger. In order to keep the same optical alignment during the measurement, we modified the tip apex by intentionally poking the tip into the clean Ag surface. The tip was moved toward the surface only by $<1$ nm, which should lead to a little change of the tip. Therefore, the background is sensitive to the atomistic structure of the tip apex. A similar correlation between the Raman intensity and the continuous background has been repeatedly observed in SERS, which is associated with plasmonic properties and chemical interactions at the interface between a sample (molecule) and a metal surface.$^4,^5$ The pronounced background suddenly appears upon APC formation, which may be related to the plasmonic field in the junction. As seen in Fig. 1f, APC formation results in a jump of the conductance, which modifies a conductively-coupled plasmon mode (charge transfer plasmon). Understanding the origin of the continuous background will be important to obtain better sensitivity.

![Figure S1](image)

**Figure S1.** TER spectra obtained for 2-ML ZnO at the APC with three different tip conditions that exhibit a different continuous background ($\lambda_{ext}=633$ nm, $F=0.39$ mW$\mu$m$^{-2}$, $t_{exp}=3$ s, 10 K).
3. Incident laser power dependence of TERS in the APC regime

Figure S2 shows the incident power dependence of TERS of 2-ML ZnO in the APC regime, indicating a linear dependence.

Figure S2. Incident power dependence of the TERS intensity measured for 2-ML ZnO (Ag tip, \( \lambda_{\text{ext}} \)=633 nm, \( t_{\text{exp}} \)=15 s, 10 K). The peak intensity at 316 cm\(^{-1}\) is plotted.
4. TERS spectra of the Ag tip–ZnO junction measured by different tips

In order to confirm the reproducibility of the distance-dependent TERS spectra, we examined more than 10 different Ag tips. **Figure S3** shows three examples from them, showing that the main features are highly reproducible.

**Figure S3.** Waterfall plot of the gap distance-dependent TER spectra recorded over 2-ML ZnO obtained by different Ag tips ($\lambda_{\text{ext}}$=633 nm, $F$=0.36 mW$\mu$m$^{-2}$, $t_{\text{exp}}$=1 s per spectrum, 10 K).
5. Details of DFT calculations

We performed density functional theory (DFT) calculations using the Vienna \textit{ab initio} simulation package (VASP),\textsuperscript{6,7} which employs the projector augmented wave formalism.\textsuperscript{8} Wave functions were expanded in terms of a plane-wave basis set with the kinetic energy cutoff of 520 eV. The Perdew-Burke-Ernzerhof (PBE)\textsuperscript{9} generalized gradient approximation was used for the exchange-correlation functional. Vibrational frequencies were calculated by using the finite difference method as implemented in the Phonopy package.\textsuperscript{5} The interface was modeled by a slab composed of \((7\times7)\) ZnO bilayer and monolayer of Ag(111) \((8\times8)\). The slab model was constructed by using the theoretical Ag lattice constant \((a=4.145 \text{ \AA})\). The \(\Gamma\) point was used for the Brillouin zone sampling. We confirmed that the structure of the interface model with the Ag monolayer does not differ significantly from that with the five Ag layers. See Ref. 6 for further details of the interface model and the DFT calculations. The Ag tip was modeled by using a four-atom pyramidal cluster.
6. **Stable structure of the Ag tip–ZnO junction**

To determine the most stable site for the Ag tip in the contact mode, we optimized the model Ag tip adsorbed on atop (Zn and O) and hollow sites of ZnO bilayer on Ag monolayer. We considered possible inequivalent sites, as the low symmetry surface structure, resulting in many inequivalent adsorption sites. We performed full optimization of the Ag tip and found that on top of the Zn and O atoms, the tip collapsed, partly because of the use of the small four-Ag-atom model tip, and that the tip remains stable only on the hollow site, suggesting that the hollow site is the most stable adsorption site for the Ag tip in the contact mode. For the atop (Zn and O) site adsorption, we fixed the top three Ag atoms of the tip and found the stable adsorption site. The most stable adsorption geometries are shown in Fig. S4.

![Optimized structures of ZnO bilayer/Ag(111) with the Ag tip at (a) Hollow site (b) atop site (Zn), and (c) atop site (O).](image)

**Figure S4.** Optimized structures of ZnO bilayer/Ag(111) with the Ag tip at (a) Hollow site (b) atop site (Zn), and (c) atop site (O).
7. Calculated charge density difference upon formation of the APC

To investigate the bond formation between Ag tip and surface atoms, we calculated the charge density difference (CDD) defined by

$$\Delta \rho(\mathbf{r}) = \rho_{\text{tot}}(\mathbf{r}) - \rho_{\text{tip}}(\mathbf{r}) - \rho_{\text{ZnO/Ag}}(\mathbf{r}),$$

where $\rho_{\text{tot}}(\mathbf{r})$, $\rho_{\text{tip}}(\mathbf{r})$, and $\rho_{\text{ZnO/Ag}}(\mathbf{r})$, are charge densities of total system, Ag tip, and ZnO bilayer/Ag interface, respectively (Fig. S5). We found that the charge rearrangement occurs between tip Ag atom and surface O atoms, suggesting the bond formation. Furthermore, we found the charges at the O sites (O#4, O#5, O#6) beneath the surface Zn atoms closest to the tip (Zn#1, Zn#2, Zn#3) are polarized suggesting the enhanced polarization at the O site.

![Image](image_url)  

**Figure S5.** Calculated charge density difference upon formation of the point contact between Ag tip and ZnO bilayer/Ag(111). Red (blue) contour is the accumulated (depleted) charge at the iso value of $3.0 \times 10^{-3} \text{e/Å}^3$. 
8. Electrodynamic simulations of the near-field distribution in the STM junction

In order to gain qualitative insight into the evolution of the in- and out-of-plane components of the plasmonic field in the STM junction (Fig. 2d in the main text), we examined the near-field distribution using electrodynamic simulations. The numerical simulations were carried out to calculate the plasmonic response of the nanotip in the STM geometry by solving the time-harmonic wave equation for the electric field in the frequency domain using the RF-Module of COMSOL Multiphysics 5.3a. The simulations were performed in 3D for a silver tip with apex diameter of \( R = 60 \) nm and we assumed a half-sphere nanoprolusion with diameter \( r = 1 \) nm (Fig. S6a and S6b). The latter mimics the atomistic structure on the tip apex. The presence of such a nanoprolusion (nanotip) is generally accepted idea to explain atomic resolution of STM. It has recently been demonstrated that the nanoprolusion plays a crucial role in field enhancement and localization in sub-nanometer plasmonic cavities,\(^{10}\) which is also assumed to explain exceptional high spatial resolution of TERS.\(^{11}\) The tip shape has an half opening angle of 6° and is truncated at a position 300 nm above the apex. The sample was modelled as a silver layer of 100 nm thickness and placed at a variable distance \( d_{\text{gap}} \) below the nanoprolusion. The 3D simulation volume was surrounded by perfectly matched layers to absorb all outgoing waves. The materials properties were set by the complex dielectric functions of gold and silver, with the values taken from the Lorentz-Drude model. Specifically, the Drude–Lorenz parameters used were taken from Ref. 12. For a given excitation frequency the model was excited by a plane wave background field linearly polarized within the plane spanned by the tip and the incoming beam and incident at an angle of 35° with respect to the sample surface. To obtain the field enhancement in the junction we used the scattered field formulation available in COMSOL Multiphysics. Simulations were performed for an excitation wavelength of 633 nm. In order to estimate the effective field component in TERS, we selected to quantify the average near field in a cylinder on the Ag surface with a radius of 0.5 nm and a thickness of 0.4 nm centered under the nanoprolusion, which are determined based on a possible spatial resolution of TERS in Å-scale gaps\(^{13,14}\) and the thickness of 2-ML ZnO.

Figure S6c displays the 2D map of the in- and out-of-plane field enhancement (\( |E_x| \) and \( |E_z| \), respectively) at different \( d_{\text{gap}} \), indicating the strong field localization at the nanoprolusion. Figure S6d shows the average field in the effective volume as a function of \( d_{\text{gap}} \). The slope of \( |E_x| \) is larger than \( |E_z| \), which is consistent with the experimental observation in Fig. 2d in the main text.
Figure S6. (a–b) Schematics of the tip-sample model for the electromagnetic simulations. (c) Two-dimensional maps of the near-field distribution for $|E_x|$ and $|E_z|$ at different $d_{gap}$. (d) $|E_x|$ and $|E_z|$ as a function of $d_{gap}$. The dashed lines are calculations for the effective cylinder radius of 1 nm.
7. Wavelength dependence of TERS in transition from the tunneling the APC regime

We found that the dramatic enhancement of the TERS intensity upon APC formation occurs at different $\lambda_{\text{ext}}$. Our previous study revealed the strong $\lambda_{\text{ext}}$ dependence in the tunneling regime and $\lambda_{\text{ext}}$ needs to match with electronic transition between the conduction band edge of the ZnO film and the interface state near the Fermi level in order to obtain the intense TERS signal. It was demonstrated that $\lambda_{\text{ext}}$=633 and 780 nm are in resonance with 2- and 3-ML ZnO, respectively.\textsuperscript{6} As shown in Figs. S7a and S7b, no TERS signal is observed for 2-ML ZnO with $\lambda_{\text{ext}}$=532 and 780 nm in the tunneling regime, whereas it becomes intense by the APC formation. Similarly, the dramatic enhancement occurs for 3-ML ZnO by APC formation at $\lambda_{\text{ext}}$=633 nm which is off-resonance in the tunneling regime (Fig. S7c). The intensity in the contact regime for 2-ML ZnO at $\lambda_{\text{ext}}$=532 and 780 nm appears to be lower than that for $\lambda_{\text{ext}}$=633 nm. However, it should be noted that, because the TERS intensity depends on the tip conditions (LSPR properties), it is not straightforward to discuss the wavelength dependence quantitatively.

![Figure S7](image)

**Figure S7.** TER spectra obtained for 2- and 3-ML ZnO at different $\lambda_{\text{ext}}$. (a) 2-ML ZnO, $\lambda_{\text{ext}}$=532 nm, $F$=0.04 mW$\mu$m$^{-2}$, $t_{\text{exp}}$=1 s, 10 K. (b) 2-ML ZnO, $\lambda_{\text{ext}}$=780 nm, $F$=0.9 mW$\mu$m$^{-2}$, $t_{\text{exp}}$=3 s, 10 K. (c) 3-ML ZnO, $\lambda_{\text{ext}}$=633 nm, $F$=0.39 mW$\mu$m$^{-2}$, $t_{\text{exp}}$=3 s, 10 K. $d_{\text{gap}}$ is indicated in the figure. The red arrows indicate the contact mode.
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