Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

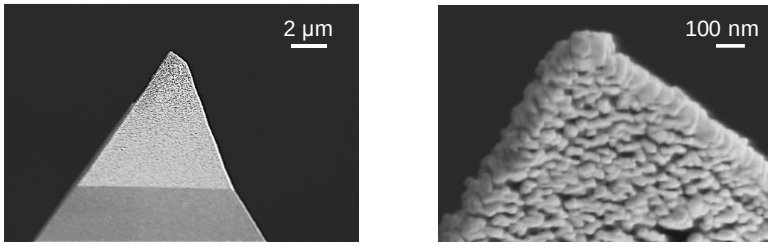
Tip-enhanced Raman Spectroscopy: Bridging the Gap between Experiments and Theory

Mahfujur Rahaman,[1] Alexander G. Milekhin,[2,3] Ashutosh Mukherjeee,[1] Ekaterina E. Rodyakina,[2,3] Alexander V. Latyshev,[2,3] Volodymyr M. Dzhagan,[1] and Dietrich R. T. Zahn[1]

1. Semiconductor Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany
2. Rzhanov Institute of Semiconductor Physics RAS, Lavrentiev Ave. 13, 630090 Novosibirsk, Russia
3. Novosibirsk State University, Pirogov 2, 630090 Novosibirsk, Russia
4. Lashkaryov Institute of Semiconductors Physics, National Academy of Sciences of Ukraine, 03028 Kyiv, Ukraine

Email: mahfujur.rahaman@physik.tu-chemnitz.de

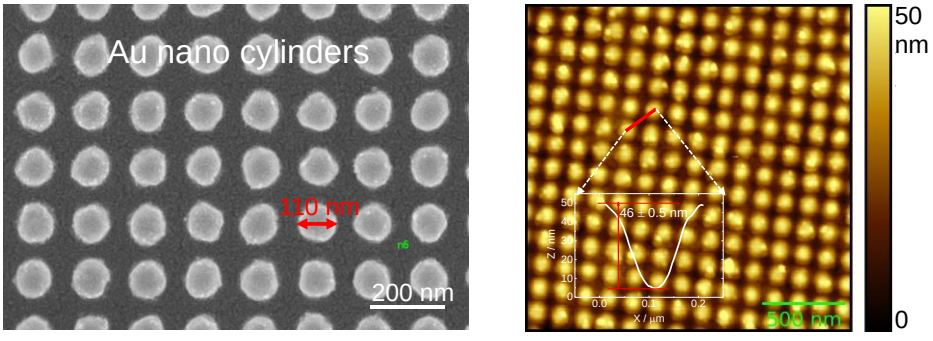
Figure S1:



(a) (b)

Figure S1: (a) A typical SEM image of a TERS tip prepared by evaporating Au on a silicon cantilever. (b) A magnified SEM image of a TERS tip revealing the formation of Au nanoclusters at and around the tip.

Figure S2:



(a) (b)

Figure S2: (a) Typical SEM and (b) AFM images of the Au nanodisks prepared by electron beam lithography. The diameter and the height of each disk are 110 nm and 50 nm, respectively. A height profile between the two disks is shown in the inset of figure (b).

Figure S3:

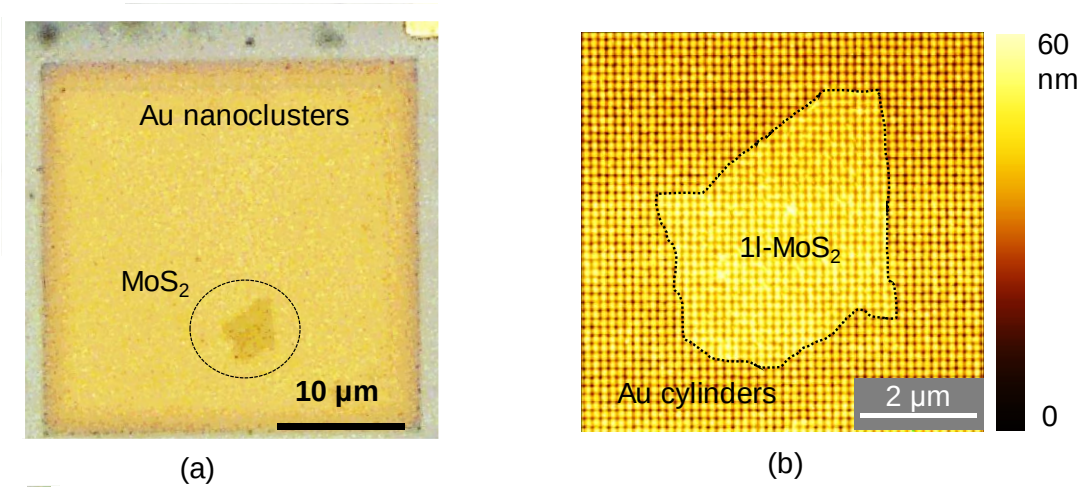


Figure S3: Optical (a) and AFM (b) images of the sample after 1L-MoS_2 flake transfer onto the plasmonic substrate (a). 1L-MoS_2 is marked by a circle in optical image and a black dotted line is made along the border of the flake as the guide for the sight.

Figure S4:

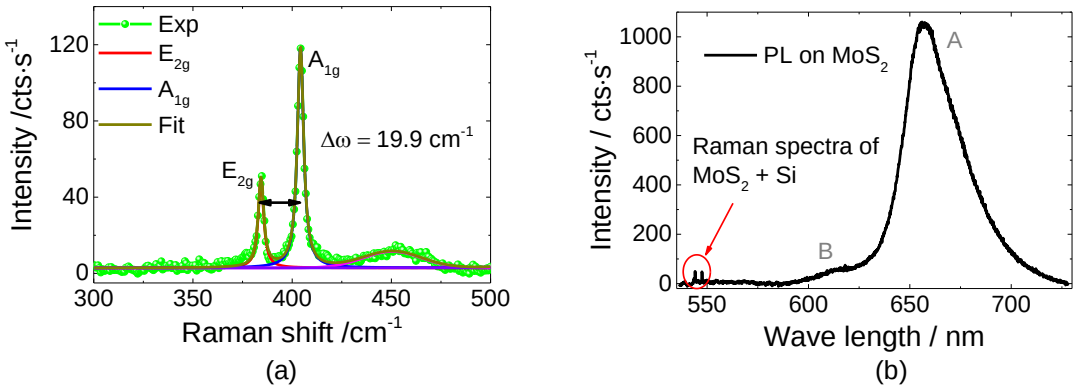


Figure S4: (a) Micro-Raman and (b) the photoluminescence spectra of MoS_2 sample shown in figure S2. The frequency difference and the high PL yield confirm the presence of monolayer MoS_2.

Figure S5:

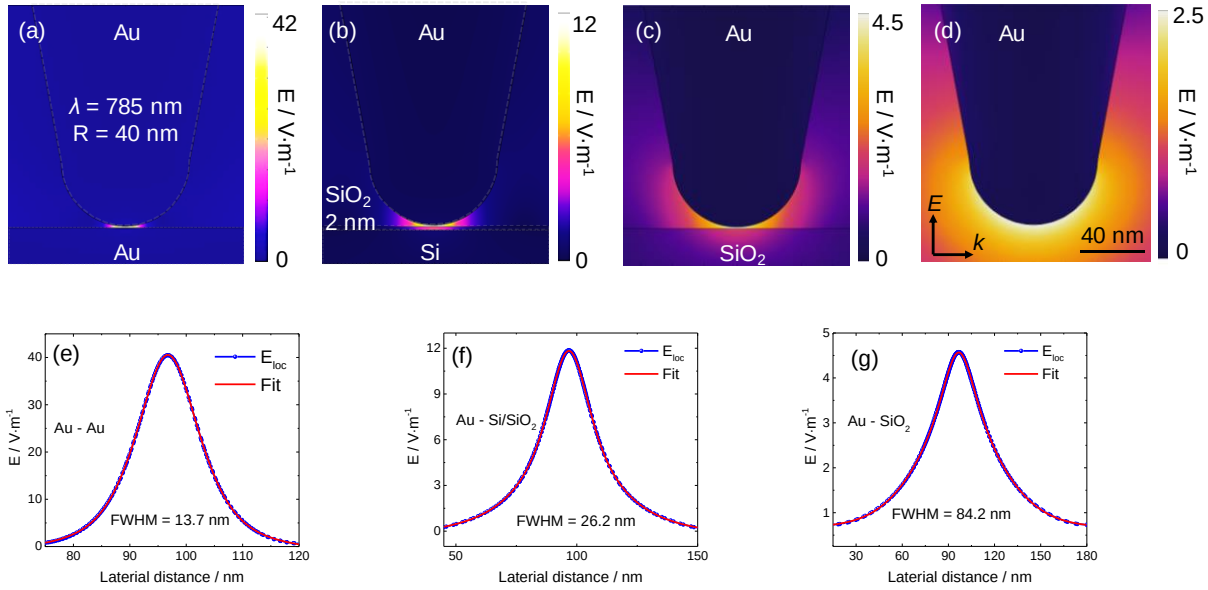


Figure S5: FEM simulation of TERS sensitivity on different substrate. TERS enhancement image of (a) Au – Au, (b) Au – (2 nm SiO_2) – Si, and (c) Au – SiO_2 tip – sample system; whereas (d) Au tip alone. The excitation energy and tip radius used I the calculation are 785 nm and 40 nm. The tip – substrate distance is kept at 1 nm for the simulation. Interestingly, even on SiO_2 substrate there is a small enhancement compared to tip alone due to slight reflective nature of the substrate originated from the change in refractive index at the air/SiO_2 interface and in agreement to the literature.[1] The electric field enhancement ratio between Au – Au and Au – SiO_2 is 9 at 1 nm tip – substrate distance. In order to determine the lateral confinement of the field, cross sections are taken along the surface line of the substrates in (a) – (c) and presented in (e) – (g) respectively.The line the shape of the lateral distribution of the fields changes from substrate to substrate and also getting narrower with increasing plasmonic interaction between the tip and substrate. Each field profile is fitted to determine the FWHM of the individual system. Compared to Au – SiO_2 system in (g), Au – (2 nm SiO_2) – Si in (f) has higher enhancement and also FWHM due to strong contribution from Si. The FWHM of Au – Au system is 13.7 nm, a very good agreement to equation 4 in the main text.

Figure S6:

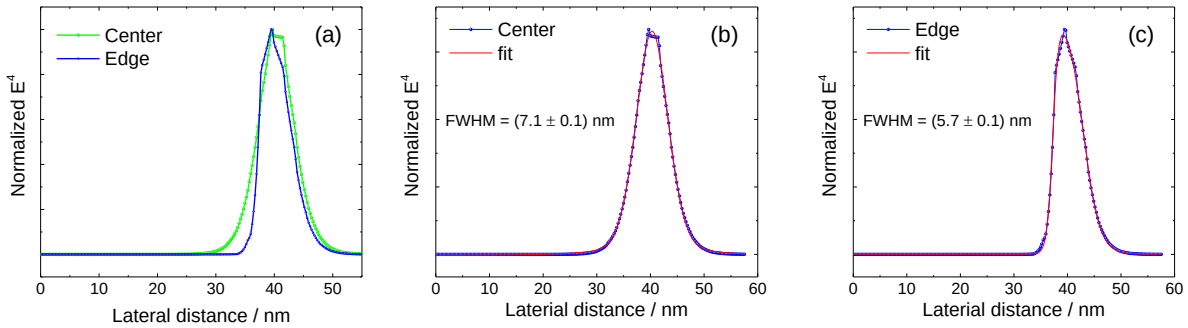


Figure S6: Influence of plasmonic substrate on spatial resolution. (a) Normalized E^4 profiles taken along the tip radius when tip is at the center and when tip is at the edge as shown in Figure 5 in main text. (b) PseudoVoigt fitting of the E^4 at the center, and (c) asymmetric Voigt fitting at the edge. As can be seen, the FWHM of the E^4 is smaller at the edge than at the center. Which implies that the spatial resolution not only depends on the product of $\sqrt{(Rd)}$ in equation 4 in the main text but also on the size and shape of the substrate.

Reference

1. S. Trautmann, J. Aizpurua, I. Go¨tz, A. Undisz, J. Dellith, H. Schneidewind, M. Rettenmayr and V. Deckert, Nanoscale, 2016, 9, 391