Chapter 1

Lithographically-prepared SERS-active substrates with well-defined gaps below 1nm

Kenneth Crozier^{1,2} and Wenqi Zhu³

*1-Department of Electrical and Electronic Engineering,
University of Melbourne, Victoria 3010, Australia*

*2-School of Physics, University of Melbourne, Victoria
3010, Australia*

*3-School of Engineering and Applied Sciences, Harvard
University, 29 Oxford Street, Cambridge, Massachusetts
02138, USA.*

Author email addresses:

kcrozier@unimelb.edu.au

1.1 Introduction

Metallic structures with nanogap features have proven highly effective for SERS, enabling an extreme level of sensitivity, down to that of single molecules [i, ii, iii]. This sensitivity comes from localized surface plasmon resonances supported by nanogaps, in which the enhancement of the electric field intensity can be as high as $\sim 10^4$. In most previous works, the general practice to model such plasmonic resonances involved the use of classical electromagnetic theory. In this Chapter, a regime is considered where quantum mechanical effects become important. It has only recently become widely appreciated amongst the nano-optics community that phenomena such as electron tunneling [iv, v, vi, vii, viii, ix] and non-locality [x, xi, xii, xiii] can appear as feature sizes approach atomic length scales. Here, we review our work [xiv] that shows unambiguously that electron tunneling at optical frequencies emerges for metallic nanostructures containing nanogaps with widths down to a few Angstroms. Of particular note for SERS is that this work experimentally demonstrates, for the first time to the best of our knowledge, that the maximum plasmonic enhancement that can be achieved is limited by the emergence of electron tunneling.

This Chapter is organized as follows. We begin by describing a method for the lithographic fabrication of gold dimers with Angstrom-scale gaps. We next describe a method for measuring the (far-field) scattering spectra of the gold dimers with gaps ranging from 10 nm down to a few Angstroms. We discuss the results, which demonstrate the impact of electron tunneling. We next describe our method for studying the impact of electron tunneling upon plasmonic near-field enhancement via SERS. This demonstration that electron tunneling limits the maximum achievable plasmonic enhancement is likely to be important for many other applications in nano-optics, in addition to SERS.

1.2 Fabrication of dimers with Angstrom-scale gaps

Electron beam lithography (EBL) allows plasmonic nanostructures to be produced with flexible designs and with controllable gap widths. Dimer structures are particularly useful for studying quantum mechanical effects in plasmonic nanogaps. They consist of pairs of metallic nanoparticles separated by small gaps. The fabrication of dimers by electron beam lithography faces difficulties for gap sizes below 10 nm [xv], although nanogaps of this size have been demonstrated using techniques that include advanced lithographic tools [xvi], special substrates [xvii] and the use of sacrificial layers [xviii]. Nonetheless, gaps below 1 nm are extremely difficult to attain using the conventional method of EBL, evaporation and the lift-off process. This is due to the resolution of the electron beam resist and other factors [xix]. We demonstrate here a two-step EBL method (Figure 1) that can produce metallic dimers separated by Angstrom-scale gaps. Our dimers comprise pairs of gold disks with diameters of 90 nm and thickness 20 nm, on a silicon nitride (Si₃N₄, 30 nm thick) window, with thin titanium (1 nm

thickness) as the adhesion layer.

Figure 1. Schematic diagram illustrating two-step EBL method for the fabrication of plasmonic dimers with Angstrom-scale gaps. Patterns produced by first EBL step are shown as solid objects. Patterns produced in second EBL step (aligned to the first) are shown as dashed objects.

The EBL tool employed is an Elionix F-125. For the first EBL exposure, we start by locating the SiN window using the scanning electron microscopy (SEM) mode of the tool. We then pattern a nanodisk array with an overall extent of $300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$, which is slightly larger than the SiN window. The nanodisks are in a square array (periodicity of $4\text{ }\mu\text{m}$). The exposed pattern also includes two alignment markers. The sample is developed, and titanium and gold are evaporated. Lift-off is performed using acetone. The second EBL exposure is aligned to the first, and contains another nanodisk array. This is not a square array, however. Rather, the locations of the nanodisks are such that perfect alignment would result in an array of dimers with gaps ranging from -40 nm (overlapped) to $+40\text{ nm}$. The gap width is designed to increase by 0.05 nm for each successive dimer, from the lower left corner to the upper right corner of the pattern. This results in dimers with Angstrom-scale gaps being achieved in the center of the pattern. We use alignment marks A and B to minimize translational and rotational errors. Typical alignment and rotational errors are below 10 nm and 1 mrad , respectively, for state-of-the-art EBL systems [xx]. Such errors make it inevitable that dimers with Angstrom scale gaps are not necessarily produced at the very center of the pattern. Nonetheless, such gaps will be produced at other places in the pattern. In the next section, we discuss their characterization.

1.3 Electron microscope characterization of fabricated dimers

As discussed, the dimers are formed on 30 nm -thick SiN membranes. This is done to enable their characterization by transmission electron microscopy (TEM). Top-view TEM images of four typical dimers are shown as Figure 2 (a)-(d). These dimers are termed Dimers I-IV, respectively. The widths of the gaps of these dimers are determined from the magnified views of Figure 2 (e)-(h). The high resolution of these images is confirmed by the fact that the atomic lattice of gold can be observed. It can be seen that there are small particles around the dimer, which is consistent with previous reports made for similar structures

[xvii]. Here, we select dimers that have no such small particles in the smallest region of the gap.

Figure 2. TEM images of dimers with atomic length-scale gap-width. (a-d) Top-view TEM images of four representative dimers I, II, III and IV with gradually increasing gap-width. (e-h) High-resolution magnified-view TEM images of gap regions of dimers of panels a-d. In panel e, nanoparticles touch, while panels f-h have gap-widths of 2.0 Å, 6.7 Å, and 5.8 nm, respectively.

To determine the widths of the gaps in a consistent manner, we employ the following process. One possible source of error is that of parallax error from sample tilting [xxi]. To avoid this, 10 TEM images are taken of each sample, with the TEM sample holder being rotated within $\pm 30^\circ$ about an axis that is in the plane of the substrate and perpendicular to the dimer long axis. We find the width of the gap for each image. The gap width is defined as the distance between the closest two points on the two disks. The gap width of a particular dimer is then taken to be the largest gap width measured from this set of TEM images. From this method, the nanodisks of Dimer I (Figure 2(e)) are found to be touching, while Dimers I-IV (Figure 2(f)-(h)) are found to have gap widths of 2.0 Å, 6.7 Å, and 5.8 nm, respectively.

1.4 Modelling the plasmonic response of nanoparticle dimers

As discussed in the Introduction, the overarching theme of this Chapter concerns the emergence of quantum mechanical effects in plasmonic dimers with sub-nanometer gaps. Understanding this phenomenon is greatly facilitated by the ability to simulate the plasmonic response of dimers using a model that does not incorporate such effects, and using another model that does. The former is the classical electrodynamics model (CEM), while for the latter we employ the quantum corrected model (QCM, [v]). In this section, we describe these modelling approaches.

We begin by discussing the method used for the CEM simulations. The geometry of the simulated structure is chosen to match that of the fabricated dimer, i.e. two gold nanodisks with diameters of 90 nm and thicknesses of 20 nm. The permittivity of gold is taken as being described by a Drude model, with $\epsilon_\infty = 1$, $\omega_p = 1.94 \times 10^{15}$ Hz, and $\gamma = 2.14 \times 10^{13}$ Hz. The TEM membrane on which the dimer sits is modelled as a 30 nm thick layer of silicon nitride (SiN) with a refractive index of $n = 2$. As discussed earlier, titanium is used to facilitate adhesion of the dimer to the membrane. TEM imaging indicates that the titanium layer is slightly (~ 2 nm) wider than the gold structure. We therefore model the titanium adhesion layer as two nanodisks with diameters of 94 nm and thicknesses of 1 nm that sit beneath the gold nanodisks. Our simulations are performed with the finite difference time domain (FDTD) method implemented in a commercial software package (Lumerical, Figure 3(a)). The permittivity of titanium is from a multi-coefficient fitting model provided by the software package. To minimize the computational workload, we make use of the symmetry in the plane of the substrate. To simulate the case of an isolated dimer, which is appropriate due to the large spacing in the fabricated array, the boundaries of the computational domain contain perfectly matched layers (PMLs) to absorb outgoing

waves. A total-field scattered-field (TFSF) source is used to realize a linearly-polarized plane wave incident on the dimer. In our experiments, dark-field scattering spectra are measured as a means for understanding the plasmonic response of the dimers. In the simulations, therefore, we place two power monitors outside the TFSF region to measure the scattering spectrum of the dimer. The meshing is as follows. The dimer structure is enclosed by a box that has a uniformly-spaced mesh of 0.5 nm. The mesh outside the box is non-uniform. For dimers with gaps narrower than 1 nm, a more finely-spaced mesh is generated within the gap region, such that the gap width corresponds to 4 unit cells. To determine the SERS enhancement factor (EF) predicted by these simulations, it is necessary to know the electric fields generated on the surfaces of the dimer. We therefore use a three-dimensional (3D) monitor with the same dimensions as the uniform mesh box to record all field data. The surface-averaged SERS EF is then found using $\frac{\iint_A |E|^2 ds}{\iint_A |E_0|^2 ds}$, where the surface A comprises all surfaces that are at a distance of 1 nm from both the top surfaces and the side walls of the dimer.

Figure 3 Simulation configurations of plasmonic dimer. (A) Side view of simulation domain in Lumerical. (B) Scheme of Drude-like tunneling region in QCM. (C) Comparison between normal incidence and oblique incidence.

The method we use for incorporating quantum mechanical effects is the QCM approach introduced by Esteban et al [v]. This approach is summarized below and enables the effect of electron tunneling to be included in classical electromagnetic calculations. Electron tunneling represents a charge transfer channel across the gap, with charges of opposite sign neutralizing each other. To implement the QCM approach, the vacuum permittivity of the gap region is replaced by a Drude model that captures the tunneling process. As indicated in Figure 3(b), different parts of the gap have different gap distances l , meaning that l is a function of (x, y) . For a certain gap distance l , the relative permittivity of the gap region is given by:

$$\varepsilon(l, \omega) = 1 - \frac{\omega_g^2}{\omega(\omega + i\gamma_g(l))} \quad (1)$$

where ω_g is the effective plasma frequency, and taken to be the plasma frequency of gold, based on the consideration that the model should resemble the Drude model of gap for gap separation $l = 0$; γ_g is the effective damping frequency, and is a function of gap distance l . The imaginary part of the permittivity is related to the conductivity in the usual manner. The conductivity is thus defined as:

$$\sigma_g(l) = \frac{\omega_g^2}{4\pi\gamma_g(l)} \quad (2)$$

On the other hand, through full quantum mechanical calculations of the probability of tunneling between two metallic parallel plates, the tunneling conductivity σ_g at a junction under bias $U = lE$ can be related to the current density J as follows:

$$\sigma_{\mathbf{e}}(\Omega) = l \frac{dJ}{dU} = l \frac{2}{(2\pi)^2} \int_0^{\Omega_F} T(\Omega, l) d\Omega \quad (3)$$

where Ω_F is the electron Fermi energy, $T(\Omega, l)$ is the energy-dependent electron tunneling probability at a lateral position within the gap for which the local separation is l . Combining Equations (2) and (3) therefore allows the separation-dependent damping frequency to be obtained. When this is performed, it is furthermore found out that γ_g generally increases exponentially with gap separation, i.e.

$$\gamma_g(l) = \gamma_g(l=0) \exp(ql) \quad (4)$$

where $\gamma_g(l=0)$ is taken as the damping frequency of gold, based on the consideration that the effective Drude model should resemble that of gold for gap separation $l=0$; and q is a material-dependent characteristic length from the exponential fit of $\gamma_g(l)$ and takes a value of $q = 2.24 \text{ \AA}^{-1}$ for gold.

With the permittivity of the gap region chosen in this way, the QCM approach allows the quantum mechanical effect of electron tunneling to be captured.

It is also important to consider a difference that exists between the illumination conditions used in the simulations and experiments. As described above, our simulation method assumes normal-incidence illumination, while in our dark-field scattering measurements, the white light source is incident at an angle of 65° . This is because the nature of the FDTD method means that oblique incidence is computationally expensive. This leads to the question of the effect of this difference in illumination conditions. To understand this, we use the finite element method (FEM) to simulate the dark-field scattering spectrum of a dimer for the case of oblique incidence (65°). The simulations are performed using the commercial software package COMSOL Multiphysics (RF module). We also simulate the dark-field scattering spectrum of the dimer under normal incidence using FEM. In Figure 3c, the scattering spectra simulated via FEM (normal and oblique incidence) are compared to the spectrum simulated by FDTD (normal incidence). These simulations are performed using the CEM approach. It can be seen that,

for normal incidence, the FEM and FDTD approaches are in general agreement. There are slight differences which we ascribe to differences in collection angles, and to differences between the dielectric functions employed. In the FEM simulations, the dielectric function of gold from Ref [xxii] is used, while in the FDTD method, the software package (Lumerical) fits the data of Ref [xxii] with a multiple coefficient model. It can be seen the spectrum under oblique incidence has a similar lineshape to that under normal incidence, but only differing in intensity. This leads us to conclude that while the FDTD simulation configuration (normal incidence) is not the same as that used in the dark-field scattering experiments (65° incidence), the difference that results is relatively minor.

1.5 Impacts of electron tunneling on far-field properties of dimer

A homebuilt dark-field microscope (Figure 4) is used to measure the dark-field scattering spectra of the dimers. White light from a halogen lamp is polarized, then loosely focused on the dimer array by a microscope objective (Nikon, ULWD, magnification $20\times$, numerical aperture NA 0.25). The polarizer is rotated so that the illumination is linearly polarized along the dimer axis. The illumination is incident at an angle of 65° from the normal to the substrate. Scattered light is collected by an objective lens (Nikon, ELWD, $50\times$, NA = 0.55) and a tube lens (focal length $f = 200$ mm), producing an image of the plasmonic dimer array at the entrance slit of the spectrometer (Acton SP2300). We then replace the entrance slit assembly with a precision pinhole (diameter $200\ \mu\text{m}$). This allows us to select the light scattered by an individual plasmonic dimer under study. The dark-field scattering spectrum S generated by the spectrometer (wavelength range: 500 nm to 1050 nm) is then recorded by the liquid nitrogen cooled charge coupled device (CCD) camera (Princeton Instruments Spec-10). An integration time of 30 seconds is used. To remove the effect of second order

diffraction from the grating in the spectrometer upon the recorded spectrum, a long pass filter (passes $\lambda \geq 532$ nm) is placed in front of the pinhole. We obtain a reference spectrum R by measuring the spectrum with the plasmonic dimer sample replaced with a white light reflectance standard (WS-1-SL, Ocean Optics). We furthermore obtain a background spectrum B by measuring the spectrum from a region on the SiN window that does not contain any dimers. With these spectra measured, the spectrum from the dimer under study is calculated as $\frac{S-B}{R}$.

Figure 4 Experimental setup for dark-field scattering spectroscopy. (a) Schematic diagram. (b). Top view photograph of set-up. (c). Side view photograph of set-up.

Using the microscope described above, we measure scattering spectra from dimers with gap widths ranging from 9.1 nm down to 2.0 Å. The results are presented as **Figure 5**. It should be noted that all optical measurements reported in this Chapter are performed prior to TEM characterization. This prevents the possibility of carbon contamination affecting the results. CEM and QCM simulations of dark field scattering spectra are presented as Figure 6 (a) and (b), respectively.

Figure 5 Measured dark-field scattering spectra from dimers with various gap-widths. Horizontal axis represents measured gap-widths from 2 Å to 9.1 nm in log scale. The scattering intensities are normalized by their largest value.

Figure 6 Simulated impacts of electron tunneling on dark-field scattering from dimers with angstrom-scale gaps. (a) Scattering intensities simulated by CEM for gap-widths from 1 Å to 10 nm. The scattering intensities are normalized by their largest value. (b) Scattering intensities simulated by QCM for same range of gap-widths as panel (a). Again, the scattering intensities are normalized by their largest value.

We now discuss the results (Figure 5 and Figure 6). According to classical plasmon hybridization theory [xxiii], there are two resonance modes, namely the bonding dipole plasmon (BDP) mode and the bonding quadrupole (BQP) mode. The simulated charge density distributions of these modes are shown in Figure 7. From Figure 5, it can be seen that as the gap width decreases from 9.1 nm to 6.7 Å, the experimentally-measured BDP resonance red-shifts from 807 nm to 892 nm, and the scattering intensity drops to 46% of its peak value. It can be furthermore seen that the measured scattering intensities of the BQP are much weaker than the BDP. Let us now consider the predictions of simulations. The CEM simulations predict that, as the gap width decreases from 10 nm to 7 Å, the BDP scattering intensity drops to 83 % of its peak value, while the BDP peak resonance shifts from 800 nm to 929 nm (Figure 6a). It can be seen from Figure 6b that the QCM-predicted scattering spectra are very similar to those of the CEM approach over this range of gap widths, due to the fact that the Drude model of the gap region almost resembles vacuum over this range.

Figure 7 Simulated charge density distributions for three plasmonic modes. (a) Bonding dipole plasmon (BDP) simulated with CEM. (b) Bonding quadrupole plasmon (BQP) simulated with CEM. These are calculated from dimer with gap-width of 9 Å. (c) BDP simulated with QCM for dimer with gap-width of 2 Å.

We next consider further reductions in gap width. It can be seen that the experimental results (Figure 5) show interesting behaviors for the BDP mode as the gap narrows from 6.7 Å (Dimer III) to 2.0 Å (Dimer II).

The scattering resonance peak no longer red-shifts, and the strength of the scattering becomes comparable to, or even smaller than, that of the BQP around 750 nm. This behavior is substantially different from what is predicted by the CEM approach (Figure 6a). However, for gaps smaller than 4 Å, the QCM approach (Figure 6b) predicts that the BDP resonance no longer red-shifts and that it drops in intensity, making the BQP mode the dominant resonance in the spectra. From Figure 5, it can be seen that these features are indeed experimentally observed for dimers with gap widths below 6.7 Å. In this regime, electron tunneling represents a charge transfer channel across the gap, with charges of opposite sign neutralizing each other, resulting in the mode shown as Figure 7c.

1.6 Impact of electron tunneling on near-field properties of dimer

We next study the effect of electron tunneling on the plasmonic near-field enhancement provided by dimers with atomic length-scale gaps. This is performed using SERS measurements. We choose this method based on the consideration that SERS enhancement factor (EF) scales roughly as the fourth power of the near-field enhancement. Self-assembled monolayers (SAMs) of thiophenol are formed on the plasmonic dimers. In Figure 8(a) and (b), TEM images of gold dimers with and without the thiophenol SAM are shown, respectively. These dimers are 40 nm thick, and have no adhesion layer. The light gray region (Figure 8(a) and (c)) that appears 1 nm wider than the gold dimer thus represents the thiophenol SAM. The gap width of the dimer of Figure 8(c) is determined to be ~ 5.7 Å. Despite the fact that this gap is very small, it can be seen that the thiophenol molecules fill the gap region (Figure 8(c)). Our estimations of SERS EF thus assume monolayer coverage of thiophenol on all exposed surfaces of the gold dimers.

Figure 8 TEM characterization of SAM of thiophenol. (a) Gold dimer with thiophenol SAM. (b) Gold dimer without thiophenol SAM. (c) Thiophenol SAM within gap region.

SERS measurements are performed using the homebuilt confocal Raman microscope (epi-configuration) shown as Figure 9. The different dimers have different gap widths, and thus different plasmon resonance wavelengths. We therefore measure SERS spectra at 19 different wavelengths (every 10 nm from 705 nm to 885 nm) for each dimer to ensure that the maximum SERS enhancement is measured. Continuous wave (CW) illumination from a Ti:sapphire laser (Mira 900, Coherent) that is tunable from 700 nm to 900 nm is used as the excitation. We keep the laser power to below 20 μ W to avoid damage to the sample. This permits multiple SERS measurements to be made, and also avoids the non-linear field enhancement that has been predicted to happen at higher intensities [xxiv, xxv]. The laser polarization is chosen to be along the dimer axis, i.e. it is consistent with the dark-field measurements from before. The beam from the Ti:sapphire laser is spatially-filtered using a precision pinhole (diameter 75 μ m). The light transmitted by the pinhole is collimated, passes through a short-pass filter, is reflected by a beam-splitter, then is focused by an objective lens (100 $\times$, NA = 0.9) into a nearly-diffraction limited spot on the sample. The beam-splitter is a pellicle beam-splitter (CM1-BP108, ThorLabs) with an 8:92 splitting ratio, i.e. it directs $\sim$ 8% of the laser beam power onto the objective. The long-axis of the dimer being studied is placed along the polarization axis of the laser beam. The sample is on a piezo-stage, allowing the dimer to be positioned at the center of the beam to maximize the intensity of the Raman scattering. The Stokes Raman scattering is collected by the objective lens, is transmitted through the beam-splitter with an efficiency

of ~92%, passes through long-pass filter, and is focused by the tube lens on the spectrometer entrance slit. The long pass filter also removes the laser line. The Raman spectra are then measured by the spectrometer, which is fitted with a CCD camera (liquid nitrogen cooled). We use integration times of 60 seconds.

Figure 9 Experimental setup for wavelength-scanning Raman spectroscopy.

We perform wavelength-scanning Raman measurements for 45 individual dimers. We present results from two representative dimers (Dimers II and III of **Figure 2**) as **Figure 10**. Based on the far-field optical measurements (Figure 5) and the high resolution TEM images, we expect that electron tunneling will occur for Dimer II, but not for Dimer III. We use our system (Figure 4) to record dark-field scattering spectra of the dimers with and without the thiophenol SAMs. For both dimers, the SAM formation results in increased scattering intensities but

with the resonance lineshapes being maintained (**Figure 10(a)-(b)**). Interestingly, it can be seen that the suppression of the BDP of Dimer II, in comparison to Dimer III, is maintained even with the formation of the thiophenol SAM. We thus conclude that electron tunneling through the SAM is still significant for such narrow gaps. The wavelength-scanning Raman measurements are shown as **Figure 10(c)** and (d). Each column of measurements shows the Raman intensity normalized by the laser power. We discuss the results in more detail in the next paragraph.

Figure 10 Dark-field scattering and wavelength-scanning SERS measurements on Dimers II and III, whose gap-widths are 2.0 Å and 6.7 Å, respectively. (a-b) Dark-field scattering spectra measured before and after thiophenol SAM formation, along with measured wavelength-dependent SERS EF, for Dimers II and III, respectively. (c-d) Intensity maps of Raman scattering from Dimers II and III, respectively. 1074 cm⁻¹ thiophenol Raman line is used to calculate SERS EFs. (e) Near-field intensity distribution simulated by QCM for ideal nanodisk dimer structure with gap-width of 2.0 Å, at its peak resonance wavelength. (f) Near-field intensity distribution simulated by QCM for ideal nanodisk dimer structure with gap-width of 7 Å.

We measure the SERS EF of the 1074 cm^{-1} Raman line at each laser wavelength for the two dimers. This permits us to quantify the SERS performance. We plot the results in Figure 10 (a) and (b). Contrary to previous reports [xxvi], our results demonstrate that the wavelength-dependent SERS EF follows the lineshape of the dark-field scattering spectra of Figure 10(a) and (b). It should be noted that our experiments differ to those of Ref [xxvi] in that ours are obtained with the incident light polarized along the axis of each dimer (both for the dark-field scattering and SERS measurements). The maximum SERS EF for Dimer II (with the $2.0\text{ \AA}$ gap) is found to be 2.4×10^8 , achieved at a laser wavelength of 815 nm. For Dimer III, the maximum SERS EF is 1.2×10^9 , achieved at a laser wavelength of 820 nm. Our results indicate that as the gap widths enter the single-digit Angstrom range, the SERS EF, and hence the field enhancement, does not increase as predicted by the CEM approach, but instead decreases.

We use the QCM approach to obtain insight into these observations by simulating the electric field intensity distributions for dimers with gap widths of $2\text{ \AA}$ and $7\text{ \AA}$. The results are shown as Figure 10(e) and (f), respectively. For each of these, the intensity distribution is plotted for the illumination wavelength for which the BDP has the largest surface-averaged enhancement. We first consider the dimer with the larger gap width ($7\text{ \AA}$). From Figure 10(e), it can be seen that only one hotspot occurs in the narrowest region of the gap, and that the maximum intensity enhancement is 7.0×10^4 . This is consistent with the near-field distribution of plasmonic dimers in the classical model [xxvii]. The situation is rather different for the dimer with the narrower gap ($2\text{ \AA}$). The QCM simulations (Figure 10(f)) predict a significant reduction in the near-field, with the maximum intensity enhancement being 1.1×10^4 . Furthermore, two hotspots occur, and the field at the gap's center is suppressed. For dimers with such small gap widths, electron tunneling becomes appreciable, providing an effective "charge transfer" channel that reduces build-up of charges of opposite signs on the two sides of the gap. This phenomenon sets an upper limit to the achievable field enhancement, and thus a limit to SER EF.

As discussed, we perform SERS measurements on 45 different dimers. Their gap widths range from 9.1 nm down to 2.0 Å. The results are shown as Figure 11a. For comparison, we use both the CEM and QCM approaches to predict the SERS EFs (Figure 11b). It can be seen that there are two regimes in Figure 11a that display opposite trends for the SERS EF as a function of gap width. For gap widths in the range from 10 nm to 6.7 Å, it can be seen that the SERS EFs generally increase as the gap width decreases. This is also consistent with the predictions made by the both the QCM and CEM simulations (Figure 11b). Let us now consider the range of gap width from 6.7 Å to 2.0 Å. It can be seen that the measured SERS EF actually decreases, rather than increases, as the gap width drops. Let us now consider the predictions of the CEM and QCM approaches. We use two models for the CEM simulations. In the first (“Model 1”), monolayer coverage of the thiophenol molecules on the gold surfaces are assumed. In the second (“Model 2”), we assume that the thiophenol molecules cannot access the narrowest regions of the gap. It can be seen (Figure 11b) that both Model 1 and Model 2 CEM simulations predict a monotonic increase of the SERS EF as the gap narrows, which is very different to what is revealed by experiments. The QCM simulations, on the other hand, predict a turning point at around 4 Å in the SERS EF vs gap width characteristics, similar to what is seen experimentally. Our results show that, in addition to reducing the scattering intensity of the BDP mode, the emergence of electron tunneling reduces the SERS EF.

Figure 11 a). Maximum SERS EFs for 45 dimers measured by wavelength-scanned SERS, shown as red circles. The horizontal error bars represents the errors in gap-width determination. The vertical error bars represents the errors in measuring SERS EFs, which is calculated from the uncertainties in reference Raman measurements for neat thiophenol. The gap-widths range from (2.0 ± 0.6) Å to (9.1 ± 0.4) nm. The maximum SERS EF measured is $(1.2 \pm 0.2) \times 10^9$ for Dimer III with gap-width of (6.7 ± 1.1) Å. b). Simulated SERS EFs using both QCM and CEM for gap-widths ranging from 1 Å to 10 nm.

1.7 Conclusions and perspectives

In this Chapter, we have described a top-down nanofabrication approach that uses lithography to produced plasmonic dimers with gap widths down to the Angstrom range. Using dark-field scattering to measure plasmonic resonances in the far-field and using SERS to measure plasmonic enhancement in the near-field, we demonstrate the effect of the emergence of electron tunneling at optical frequencies. Our work demonstrates that the maximum achievable plasmonic enhancement is limited by electron tunneling. A long-held assumption in SERS has been

that smaller that smaller gaps in metallic dimers are always beneficial for field enhancement. Our work runs counter to this.

In closing, we note that our work is part of growing research field concerned with quantum mechanical effects in plasmonic structures with gaps below 1 nm [xxviii]. Interest in this topic is motivated by the importance of field enhancement for many plasmonic applications, and thus by the curiosity of many researchers regarding its fundamental limits. In addition, possibilities for the control of electron transport afforded by sub-nanometer gaps present a means for tuning the plasmon resonances of a structure [xxix]. There are also exciting prospects for nanoscale light sources via the coupling between tunneling electrons and photons [xxx, xxxi]. In our study, we use electron beam lithography to produce sub-nanometre gaps. Yet other groups have developed innovative alternatives to achieve the same goal. Savage et al [vi] demonstrated gap widths in the tunneling regime by pushing gold-coated atomic force microscope (AFM) cantilever tips together, with physical contact indicated by the differential tunneling conductance G exceeding the quantum conductance $G_0 = \frac{2e^2}{h}$ (where h is Planck's constant and e is the elementary charge). Scholl et al [vii, xxxii] used electron beams to manipulate plasmonic nanoparticles with sizes up to ~ 25 nm via Coulomb forces. Sub-nanometer gaps have also been achieved via bottom-up approaches based on inorganic two-dimensional van der Waals spacer materials [xxxiii] and using small surfactant molecules [xi, xxxiv, xxxv, xxxvi, xxxvii]. In our study, we monitor plasmon resonances in the far-field using dark-field scattering spectroscopy. Other groups have also employed this method [vi, xi], while other have used electron energy loss spectroscopy (EELS, [vii, xxxii]). In our study, we quantify near-field enhancement using SERS. Yet others have employed photoluminescence [xxxviii], four-wave mixing [xxxix] and third harmonic generation [xl] toward this goal. Despite recent advances in this field, there is much more to be done. There are many fundamental questions to be explored and many potential applications awaiting realization. We thus anticipate that quantum mechanical effects in plasmonic structures with gaps below 1 nm will be a fertile research topic in the years to come.

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Author/s:

Crozier, K;Zhu, W

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