Molecular electronic plasmonics

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\textbf{ABSTRACT}

Molecular electronic plasmonics (MEP) is an area of research that utilizes the electronic properties of molecules to control and modulate surface plasmons and holds the potential to develop on-chip integrated molecular-plasmonic devices for information processing and computing. Combining molecular electronics with plasmonics gives the opportunity to study both charge transport in molecular electronic devices and plasmonics in the quantum regime. Here, we review the recent progress in molecular electronic plasmonics and mainly focus on the areas of quantum plasmonics, and plasmon excitation and detection. This review also identifies challenges that need to be resolved to drive this field forward including improving models aimed to advance our understanding of electron-plasmon interactions in the quantum tunneling regime. Future progresses can be expected towards incorporating functional molecules to actively control MEP devices and integration of MEPs with other circuit components.

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1. Molecular electronics and surface plasmons

Nano-electronic circuits provide the ability to control charge transport at the nanoscale but data processing and transportation speeds are limited at their GHz bandwidths [1–3]. Photonic elements can carry information with a capacity exceeding 1000 times (> THz) that of electronic components, however the relatively large wavelength of light requires optical components to be too large to compete in size with modern day nanoelectronics [2–5]. With the ability of subwavelength confinement and large bandwidth (>100 THz), surface plasmon polaritons (SPPs) in metallic nanostructures have the potential to be integrated with nano-electronic circuits resulting in a true hybrid of optics and electronics at the nanoscale [2–7].

Molecular electronics utilizes single molecules or self-assembled monolayers (SAMs) as electronic components in molecular junctions consisting of 2 or 3 electrodes [8–17]. The mechanism of charge transport across such molecular junctions is

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quantum mechanical tunneling, and thus metal–molecule–metal junctions are often called molecular tunnel junctions (MTJs) or SAM-based tunnel junctions (STJs). Recent experiments in MTJs and STJs have advanced our understanding of the mechanisms of charge transport across such junctions significantly and lead to experimental demonstrations of conductance switching [18–21], rectification of currents [17,22–27], quantum interference [28–31], negative differential conductance [32–34], magneto resistance [35–39], or optoelectronics [40–45].

Surface plasmon polaritons (SPPs) are collective oscillations of electrons at the metal–dielectric interface [6]. Surface plasmons are able to confine light beyond the diffraction limit [7] at the nanoscale to form localized surface plasmons (LSPs) [46–50] and propagating SPPs [51–56]. Benefitting from the strong field enhancement at the surfaces of metallic structures, surface plasmons are suitable for sensing at the single molecule level [57–64]. Besides sensing, SPPs are also promising in other areas including sub-diffraction imaging [65–70], energy harvesting [71–76], nonlinear optics [77–82], and nano-optoelectronics [83–87]. To further promote local field enhancement, plasmonic resonators have been placed in close proximity with each other down to a few nanometers [88–102] and reach the quantum mechanical tunneling regime [89,91,93–97,101,102], i.e., the regime where changes can tunnel between the two plasmonic structures. This regime is also the length scale where molecular electronics operates and thus it seems a natural choice to study the relation between plasmons and molecular electronics.

Here, we review the recent developments and progresses of molecular electronic plasmonics (MEP). Fig. 1 shows that in principle three types of MEP devices can be identified. Although this figure depicts the electrodes as spherical plasmonic resonators, one or both electrodes can also be planar macroscopic electrodes.

1. Molecular electronics applied in quantum plasmonics (Fig. 1a).
   Two closely spaced plasmonic resonators are bridged by a SAM onto which plasmons are excited by incident light or by an electron beam. The plasmons induce an electric field in the gap which drives quantum mechanical tunneling between the two resonators resulting in quantum plasmon resonances (QPRs) such as the so-called charge transfer plasmon (CTP) modes [103–112].

2. Molecular electronics applied in plasmon excitation (Fig. 1b).
   These molecular electronic junctions are based on two electrodes of which at least one supports plasmons separated by a SAM or even a single molecule. An applied bias across the gap induces tunneling between the electrodes which result in the excitation of plasmons either by direct tunneling or via electroluminescence from the molecules inside the junctions.

3. Molecular electronics applied in plasmon detection (Fig. 1c). The same junction shown in Fig. 1b can also be used to detect plasmons. Here, plasmons are excited in the junction via an external light source. These plasmons couple to the tunneling charge carriers and increase the tunneling current across the junction making it possible to detect plasmons.

A simplified form of the Simmons equation (Eq. (1)) [113] is commonly used to approximate molecular tunnel junctions and shows how the tunneling rate $J$ (A/cm$^2$) relates to the tunneling barrier width $d$ (in nm) and height $\varphi$ (in eV).

$$J = J_0 e^{-\beta d} \text{with } \beta = 2 \sqrt{\frac{2m_e \varphi}{\hbar^2}}$$  (1)

Here, $\beta$ (Å$^{-1}$) is the tunneling decay coefficient, $J_0$ is pre-exponential factor (A/cm$^2$), $m_e$ is the effective mass of an electron (in kg), and $\hbar$ is the reduced Planck’s constant. The value of $\beta$ determines how quickly the measured value of $J$ decays as a function of $d$ and depends on the molecules inside the junctions which determine both the values of $d$ and $\varphi$. In molecular electronics it is well-known that conjugated molecules have relatively small HOMO–LUMO gaps (HOMO= highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) resulting in
low tunneling barrier heights as schematically indicated in Fig. 1d. Because of the shallow tunneling barrier, the value of $\beta$ is low (0.1–0.3 Å$^{-1}$ [10,12,114]) and coherent tunneling may be observed over large distances of up to 4–5 nm [8–10,115–119]. In contrast, aliphatic molecules have relatively large HOMO–LUMO gaps of 8–9 eV resulting in large tunneling barrier heights (Fig. 1e) and $\beta$ values of 0.8–0.9 Å$^{-1}$. Consequently, the tunneling rates across these junctions are smaller than across junctions with conjugated molecules of equivalent length [11,114,120]. Likewise, tunneling through vacuum is inefficient ($\beta=2.9$ Å$^{-1}$ [11,120]) and tunneling phenomena can be ignored in plasmonic systems involving distance larger than 1 nm [106,110]. For these reasons, molecular tunnel junctions [8–45] are interesting candidates for applications in MEP.

2. Molecular electronics applied in quantum plasmonics

Quantum plasmonics studies the interaction between light with quantum properties (e.g., single photon sources) and matter supporting plasmons [121–125]. Recently, quantum plasmonics also studies plasmon modes induced by non-local [126–135] or quantum mechanical tunneling phenomena [103–112] between near-touching (e.g., gap < 5 nm) plasmonic dimers. Plasmonic dimers have attracted intense interest because of the enhanced field enhancements due to coupled plasmons in the dimer junctions, leading to surface enhanced spectroscopies enabling single molecule detection [88–102]. Classical calculations predict that large charge densities can be induced at the opposite sides of a plasmonic dimer with a small gap, leading to large field enhancements at the gap and strongly red-shifted bonding dimer plasmon (BDP) resonances [126,127]. However, these classic calculations do not take non-local effects (the spill out of the electron charge distribution) and possible electron tunneling across the plasmonic dimer into account. The nonlocal dielectric response and tunneling effects cause a blue-shift (or less pronounced red-shift) of the BDP resonances and reduce field enhancements relative to classical local calculations [103–112,126–135]. Electrons tunneling at subnanometer gaps at sufficiently high field strengths will lead to a new resonance mode, the charge-transfer plasmon (CTP) mode [103–112].

2.1. Quantum plasmon theory

Most theoretical investigations of plasmon resonances use classical electromagnetic models (CEM) which are based on Maxwell’s equations with a frequency-dependent local dielectric function $\varepsilon(\omega)$ for each part of the nanostructure [126,127]. The CEM model uses a classical local approach, i.e., $\varepsilon(\omega)$ at the interface between different materials changes abruptly and is valid for most plasmonic systems with large values of $d > 5$ nm [110].

When $d$ reduces to the nanometer or even sub-nanometer scale the electron density spill-out or the possible inter-structure electron tunneling cannot be ignored and the local dielectric function $\varepsilon(\omega)$ will not change abruptly at the interface [128–135]. Thus, a full quantum mechanical treatment of such plasmonic system is required. However, because of the large number of atoms (e.g., a 20 nm gold sphere consists of ~25000 atoms) involved in typical plasmonic systems, it is currently not possible to address this problem with first-principle methods [128,131]. Instead, such systems have been modelled with a classical non-local model [128–135] pioneered by Pendry, Maior, and García de Abajo et al. or the quantum corrected model (QCM) developed by Aizpurua, Nordlander, and Borisov et al. [103–112]. In the classical non-local calculations, the metal response is described using the hydrodynamic non-local approach but without considering charge transfer across the dimers [110]. While in the QCM calculations, the metal is described using a classical local dielectric constant and taking electron tunneling across the dimer gap into account [110]. Based on the way to describe the electron tunneling process, the QCM model has been further classified into volume-based QCM [103–110] which uses artificial dielectric materials in the whole gap and boundary-element-based QCM [112] which uses nonlocal boundary conditions only at the surfaces of the dimer gap (Fig. 2a).

Fig. 2b shows the general results of the classical local, classical non-local, and QCM models, for plasmonic dimers separated by vacuum [110]. In the local regime ($d > 5$ nm), all these methods give the same result. In the non-local regime (0.3 nm < $d < 5$ nm), both the classical non-local and the QCM methods give similar results and predict the BDP modes red-shift less than predicted by local method. In the quantum mechanical tunneling regime ($d < 0.3$ nm), QCM predict CTP modes at $d = 0.3$ nm where tunneling happens and the spectra blue shift as $d$ decreases. The classical local and
classical non-local methods only observe CTP modes for \( d \leq 0 \text{ nm} \) (i.e., touching dimers), here the CTP mode is supported by conduction through the metal contact and not tunneling. In addition to blue-shifted extinction spectra, QCM also predicts a decreased field enhancement in the dimer gap when the plasmonic dimer reaches quantum regime at \( d < 0.3 \text{ nm} \).

It is worth noting that the classical non-local modeling is usually performed using the finite element method (FEM) with the hydrodynamic Drude model to describe the dielectrics of the metal. While the volume-based QCM is performed using the boundary element method (BEM) with the artificial dielectric materials calculated by the time-dependent density functional theory (TDDFT). The boundary-element-based QCM uses modified nonlocal boundary conditions instead of TDDFT calculations to simplify the simulations and shows similar results as the volume-based QCM.

Fig. 2c and d shows the typical plasmonic resonances of a gold nanoparticle dimer (diameter 50 nm with an air dimer gap) at the near-touching regime calculated by CEM and QCM respectively [106]. There are several main observations. The QCM calculations show a smaller number of modes than the CEM calculations because the Fabry-Perot resonances in QCM are less pronounced due to large damping raised by electron tunneling in the inter-structure junction. The QCM calculations show that a first order CTP mode (defined as tunneling CTP mode or tCTP mode) and higher order CTP mode are observed for \( d < 0.3 \text{ nm} \) where the electron tunneling becomes important (we note that the value of \( d \) at which tunneling rates are high enough to observe CTP modes depend also on the tunneling barrier height; see Fig. 1). In other words, when the air gap decreases to below 0.3 nm, the BDP switches to CTP mode with the following features: the resonance peak blue shifts (instead of red shifts) and the peak intensity decreases when electron tunneling becomes more pronounced with decreasing values of \( d \) because the electron tunneling reduces the plasmonic coupling by screening the surface charges of localized plasmons. In addition, the CTP mode happens at infrared frequencies (<1 eV) with a low resonance intensity. As the infrared resonance is far from the resonance frequency of the plasmonic resonator, the tCTP mode is mainly due to the oscillation of electron tunneling. These behaviors of both BDP and CTP modes around the \( 0.3 \text{ nm} \) air gap are the indication of the quantum plasmon resonances.

As the tCTP mode originates from the electron tunneling across the dimer, the tCTP mode directly depends on the gap conductivity, i.e., tunneling current density, raised by the plasmonic fields in the gap. Fig. 2e shows that the tCTP mode switches to a lower frequency resonance when the tunneling reaches the Fowler-Nordheim regime [108]. Because the tunneling current and the CTP mode are induced by the plasmonic fields, the CTP modes should also be sensitive to the geometry of the plasmonic dimer. Fig. 2f shows that this is indeed the case and that there is no clear CTP mode in a plasmonic dimer with a flat gap (modelled using two cylindrical plasmonic structures) as the longitudinal antenna plasmons (LAP) and the CTP have almost the same resonance frequency [109].

### 2.2. Quantum plasmonics with air/vacuum tunneling barriers

Quantum plasmonics have been studied with plasmonic dimers containing air/vacuum tunneling barriers. As discussed above, to identify quantum plasmon resonances, plasmonic dimers separated by air or vacuum gap of \( \sim 0.3 \text{ nm} \) are needed. Such structures are extremely difficult to fabricate using top-down lithography methods such as electron-beam lithography (EBL). Fig. 3a shows the plasmonic resonances, measured by electron energy loss spectroscopy (EELS) inside a transmission electron tunneling microscope (TEM), of bowtie antennas fabricated by EBL with different values of \( d \) [136]. The CTP mode was observed for touching structures, but these structures did not reveal the BDP to CTP mode transition or the tCTP mode likely because the value of \( d \) of \( \sim 0.5 \text{ nm} \) was too large to enter the quantum mechanical tunneling regime. Savage et al. [137] used a conducting atomic force microscope (AFM) equipped with two gold-sphere modified probes to form plasmonic dimers. These authors controlled the tunneling current between the AFM tips in air and simultaneously measured the dark field scattering spectra of the junction (Fig. 2c and d). As the value of \( d \) decreased, the BDP modes first red shifted with decreasing \( d \) but then blue shifted for \( d < 0.3 \text{ nm} \) which demonstrates the quantum behavior of the plasmonic resonance. Scholl et al. controlled \( d \) of two gold nanospheres inside a TEM and measured their resonance properties with EELS [138]. They also observed the BDP to CTP transition when the gap of the gold nanoparticle dimer is \( \sim 0.27 \text{ nm} \) which is a clear signature of the quantum plasmon resonance. However, in both cases (Fig. 3b and c) [132,133], the tCTP mode could not be directly observed likely due to the limited spectral range in their experiments.
2.3. Quantum plasmonics with molecular tunneling barriers

Quantum plasmonics have also been studied with plasmonic dimers containing molecular tunneling barriers. To form sub-nanometer plasmonic dimers, SAMs are promising candidates because of the ease at with which $d$ can be controlled by simply changing the molecular length of the molecules inside the SAM greatly simplifying the fabrication of structures with small values of $d$.[130,139–141]

The quantum plasmon behavior of BDP mode was first investigated using gold nanoparticles (Au NPs) deposited on a SAM of amine-alkanethiolates ($\text{S-(CH}_2\text{)}_n\text{NH}_2$) supported on a gold film.[140] By simply changing the value of $n$, the authors could control $d$ at the atomic level one CH$_2$ unit at a time and the BDP mode red shifted with decreasing $n$. This red shift was not as pronounced as predicted by CEM but the experimental data fitted well using nonlocal dielectric functions of Au. In this experiment, the transition from the BDP mode to the CTP mode—the key signature of entering the quantum regime—was not observed perhaps due to the relatively large value of $n = 2–16$, and the large HOMO–LUMO gap (~8–9 eV) of amine-alkanethiolates resulting in large tunneling barrier heights (Fig. 1e). Nevertheless, this experiment confirmed the nonlocal contribution to surface plasmon scattering.

The quantum plasmon behavior of BDP mode was confirmed with a junction consisting of two gold nanospheres separated by a SAM of alkanedithiolates ($\text{S-(CH}_2\text{)}_n\text{-S}$) shown in Fig. 4b.[139] This Au NP based junction has more confined and pronounced gap plasmon modes than the Au NP–SAM-Au film junction described above (Fig. 4a) which may facilitate the electron tunneling driven by the local plasmonic fields. The resonance peak of the BDP red shifted with decreasing $n$, but it blue shifted for $d < ~1$ nm (or $n < 5$) which strongly indicates the transition of BDP to CTP mode, a clear signature of quantum effects in the plasmonic resonance in these structures.

The ICTP mode could be directly observed in junctions consisting of two silver nanocubes separated by SAM of 1,2-ethanedithiolates (EDT) or 1,4-benzenedithiolates (BDT; Fig. 4c)[140]. The Ag nanocubes had atomically flat facets and large cross-sectional areas (~$10^3$ nm$^2$) for tunneling which increased the number of tunneling events across the junctions and enhanced the weak ICTP mode. The plasmonic resonances of the dimers were characterized using EELS inside a TEM, which provided the possibility to correlate the spectra to the gap size. As shown in Fig. 4c, the ICTP mode was observed as a new low energy peak at 0.5 eV. Because the conductance of the BDT SAM was higher compared to the EDT SAM, the resonance peak of the ICTP mode shifted from ~0.6 eV to ~1.0 eV while keeping the value of $d$ equal (considering the similar lengths of BDT and EDT). This shift in the ICTP energy was related to the reduction of the tunneling barrier height as EDT has a larger HOMO–LUMO gap (8 eV) than BDT (5 eV) as depicted in Fig. 1. Since the conjugate BDT SAMs support high tunneling rates, the ICTP mode could be observed even for values of $d$ up to 1.3 nm. The molecular electronic control over the BDP mode (coupled plasmon resonance) was confirmed in Au NP–SAM-Au film junctions with SAMs of BPD (biphenyl-4,4′-dithiolate) and BPT (biphenyl-4-thiolate) by Benz et al.[4] Here the BPD molecules have a larger conductivity than BPT molecules and consequently the BDP mode was blue shifted ~50 nm by simply replacing the BPT SAM by a BPD SAM. In this example, $d$ and the refractive indices of both SAMs were very similar and thus the change in the tunneling rate defined by the molecule caused the change in the optical properties of the junctions.
3. Molecular electronics applied in plasmon excitation

Plasmons can be electrically excited by two approaches which we define as direct and indirect plasmon excitation as shown in Fig. 5. Direct plasmon excitation relies on plasmon excitation by tunneling electrons directly. In other words, the tunneling current directly couples to plasmon modes in, for instance, metal–insulator–metal junctions [142–149]. Indirect plasmon excitation relies on two steps. First, charge carriers induce the electron–hole pair generation in the junction which then recombine and emit a photon. Second, these emitted photons then excite plasmons. Although many examples of indirect plasmon sources are based on the electroluminescence of semiconductors (e.g., light emitted diodes [150–153], silicon particles [154], or carbon nanotubes [155]), here we only focus in indirect and direct plasmon sources based on molecules.

3.1. Mechanisms of plasmon excitation in tunnel junctions

When a tunneling current flows through a junction, plasmons are excited in the plasmonic electrodes (usually made of Au or Ag). This plasmon excitation process has been often assumed to proceed via inelastic tunneling [142–149,156–158]. The schematic diagram of inelastic tunneling is shown in Fig. 5a. During the tunneling process, most of the electrons tunnel elastically, however, a small portion of the electrons tunnel inelastically and excite plasmons in the tunnel junctions. The first example of a direct plasmon source was reported by Lambe and McCarthy in 1976 [142]. They observed broadband light emission from planar metal–insulator–metal (MIM) tunnel junctions (Al–Al2O3–Ag/Au) from radiatively decaying plasmons. The color of the light depends on the applied bias $V_{\text{appl}}$ and the high frequency cutoff of the optical spectra follows the quantum relation $\hbar \nu_{\text{cutoff}} = e V_{\text{appl}}$. Since their experiments, plasmons have been excited in different types of tunnel junctions including MIM tunnel junctions based on metal–oxide insulators [144–146], air gaps [147,148], hexagonal boron nitride (hBN) [149], and scanning tunneling microscopes (STMs) [156–183].

Often, the photon-assisted tunneling model has been used to explain how charge carriers couple to plasmons (see Section 4.1). This model implies that the emitted photon from the junction cannot exceed the electron energy of the applied bias $V_{\text{appl}}$ and $\hbar \nu_{\text{cutoff}} = e V_{\text{appl}}$ applies (Fig. 5c). Schull et al. reported that quantum shot noise becomes important for tunnel junctions with high tunneling currents close to the quantum conductance $G_0$ [162,164]. These junctions emit photons with energies larger than $e V_{\text{appl}}$ (Fig. 5c). Later, Nitzan et al. established the theoretical link between the quantum noise and the ac conductance of the tunnel junction, and the plasmonic light emission based on the nonequilibrium Green function formalism [171]. The shot noise directly excites the plasmonic resonance of the tunnel junction through its spectral distribution at the optical frequency. The model also explains that photons are emitted with higher energy than $e V_{\text{appl}}$ because of strong electron–electron coupling (Fig. 5c).

In molecular tunnel junctions so far, plasmons have been excited, or modulated, using electroluminescent molecules. Fig. 5b shows that electrons and holes are injected in the molecule which then recombine and emit a photon [174–183]. Plasmons can also be excited via direct tunneling between the substrate and the tip and the challenge is to discriminate between plasmons excited via the photons emitted from the molecule or via direct tunneling. The energy levels of molecules (e.g., HOMO or LUMO) may participate in the tunneling process and thus affect the plasmon excitation process. Therefore, in systems with low lying energy levels the mechanism of plasmon excitation can be challenging to determine.

3.2. STM-based molecular electronic plasmon sources

The highly localized tunneling current in the STM make it possible to excite plasmons locally with a sub-nanometer resolution. Pioneering experiments by Coombs, Gimzewski and Berndt et al. [156–158] showed broadband light emission from STM junctions on different (polycrystalline Ag, Au [110], Cu(111), and Ag(111)) metallic surfaces. Here, inelastic tunneling electrons excited LSPs between the proximity of the tip and the sample; these LSPs then radiatively decayed and were detected optically by placing objectives nearby the junction. Since then, plasmon excitation in STM junctions have been intensively studied both experimentally and theoretically [159–173]. These studies showed that the geometry of the tip is important in the plasmon excitation [172,173], enabled sub-nanometer resolution plasmon mode mapping [159–161], and improved the understanding of plasmon excitation by coupling the local density of electronic and optical states [163]. By integrating the STM with an inverted optical microscope, SPPs excited by STM junctions have been directly imaged through leakage radiation microscopy [165–170].

During the last decade, indirect plasmon excitation via the electroluminescence of molecules has been investigated [174–183]. In these systems it is important to decouple the molecule from the metallic surfaces to avoid quenching. In practice, this decoupling has been realized by isolating fluorophores from metallic substrates using thin (in)organic insulating layers such as metal oxides [174,177], or molecular layers [175,176]; these types of junctions have been recently reviewed in detail elsewhere by Shamaia et al. [40], Galperina et al. [41], and Rossel et al. [178].

Instead of using insulating layers to decouple the molecules from the bottom-electrode, recently “molecular” approaches have been used to minimize quenching. Usually, unmodified porphyrins lie flat on metal surfaces because of strong molecule–substrate interactions. Fig. 6a shows a porphyrin molecule with a rigid tripod anchor and spacer to effectively place the porphyrin away from the bottom-electrode [181]. Fig. 6b shows the STM-induced luminescence spectra which are characteristic for the porphyrin moiety proving effective decoupling of the porphyrin from the bottom-electrode although electroluminescence intensity from these molecules was about one order of magnitude lower than that of the bare substrate. This reduction in the luminescence intensity may be due to the reduced plasmon fields due to the large tip–substrate distance or the non-radiative decay channels related to charge transfer or dipole–dipole energy transfer. Although the decoupling of the porphyrin molecule is successful, further understanding and the recovery of the luminescence intensity is needed.

Another decoupling experiment has been realized by simply lifting a polythiophene wire with a STM tip from a gold surface (Fig. 6c and d) [182]. During the experiment, the polythiophene wire was lifted off from the Au surface by several nanometers using the STM tip, so the wire ends were directly connected to the electrodes, whereas a part of the polymer chain was suspended inside the junction and disconnected from the substrate. The STM-induced luminescence spectra from the suspended wire showed a broad resonance whose maximum did not shift with voltage. These voltage independent spectra were believed to be the electroluminescence of the suspended wires by the recombination of electrons injected from the tip in the LUMO with holes injected from the sample in the HOMO of the wire junction. This experiment introduced a new experimental method to decouple molecules from metallic substrates by simply lifting up the molecules, although the electronic properties of the junctions is not completely clear as the tip geometry, molecule-tip and molecule-substrate interactions, or conformation of the molecule inside the junction, are not known.

Besides molecule-specific electroluminescence, individual molecules could also influence the plasmon excitation in STM...
Fig. 5. Molecular electronics applied in plasmon excitation. (a,b) Schematics of direct (a) and indirect (b) plasmon excitation in tunnel junctions, respectively. The molecule can modulate the inelastic tunneling by their electronic transitions between HOMO–LUMO orbitals. (c) The left panel show the junction conductance as a function of tip-substrate distance. The right panel shows the light emission spectra as a function of the distance between the Au tip and Au substrate. When $G/G_0 > 0.3$, the spectra fall in the $hv < eV$ (inelastic tunneling regime), but for $G/G_0 < 0.3$, photon energies with $hv > eV$ are observed (quantum shot noise dominated regime). Adapted from Ref. [162].

3.3. On-chip molecular electronic plasmon sources

Electrically-driven on-chip plasmon sources are essential for integrated plasmonic circuits. Recent efforts mainly relied on indirect electrically-driven plasmon sources based on miniaturized light sources that exploit electroluminescence from nanoscale semiconductors such as nano-light emitting diodes or carbon nanotubes [150–155]. However, these plasmon sources are limited in speed because they rely on electron-hole recombination which typically occurs on the nanosecond time-scales. Direct electrical excitations of plasmons in tunnel junctions occur at the quantum mechanical tunneling timescales and are thus fast [184]. In principle, MIM junctions are compatible with on-chip applications, but so far they have not been coupled to plasmonic waveguides. Recently, MIM junctions based on hexagonal boron nitride or vacuum as the insulator have been combined with optical antennas [147–149].

We recently reported on-chip direct plasmon excitation using molecular tunnel junctions based on SAMs [185]. We found that the plasmons in these junctions originate from single, diffraction-limited spots, follow power-law distributed photon statistics, and have well-defined polarization orientations which are controlled by the tunneling direction defined by the tilt angle of the SAM or by simply changing the applied bias of the junction. Fig. 7a shows the schematic of the STJ which consists of an EGaIn/Ga$_2$O$_3$ top electrode confined in a through-hole in a transparent rubber (polydimethylsiloxane; PDMS) and an ultra-flat template-stripped Au (Au$_{13}$) electrode supporting SAMs of SC$_{12}$. These junctions excited both localized and propagating SPPs (Fig. 7b and c). In the real plane image (Fig. 7b), LSPs are characterized by diffraction limited emission spots and the SPPs by the unidirectional and un-diffracted emission spots around the boundary of the junction. In the back focal plane image (Fig. 7c), the SPPs are shown as narrow arcs with specific wavevectors $k_{SPP}$ and labelled with mode I (SPPs along the Au/SAM—Air interface, $k_{SPP} = 1.01$) and II (SPPs along the Au/SAM—PDMS interface, $k_{SPP} = 1.47$). Fig. 7d shows the defocused plasmon emission image of Fig. 7b which indicates the polarization orientation of the plasmon emission spot. Theoretical calculations confirm that the polarization orientation of the plasmon emission is $\sim 30^\circ$ with respect to the surface normal and equals to the tilt angle of the SAMs. This relation implies that the plasmon excitation in the STJs occurs along the tilted back bone of the SAM via through-bond...
Fig. 6. Molecular electronics applied in plasmon excitation in STMs. (a,b) Electroluminescence modulated plasmon excitation in a STM junction with a fluorophore from the bottom electrode by intra molecular spacer. Adapted with permission from Ref. [181]. Copyright 2013 ACS. (c,d) Electroluminescence modulated plasmon excitation in a STM junction with a suspended electroluminescent oligomer. Adapted with permission from Ref. [182]. Copyright 2014 APS. (e,f) Molecular orbital gated plasmon excitation in a STM junction with Ir(ppy)₃ adsorbed on a monolayer of C₆₀. Adapted with permission from Ref. [183]. Copyright 2013 ACS.

Fig. 7. On-chip plasmon excitation with STJs. (a) Schematic of the on-chip STJs. Here, the substrate is glass, OA is an optical adhesive that was used in template-stripping. AuTS is template stripped Au, PDMS is polydimethylsiloxane based rubber mold with microchannels that stabilizes the top electrode, EGaIn stands for eutectic alloy of Ga and In, and Ga₂O₃ is a native, conductive oxide surface layer of 0.7 nm on the EGaIn. (b,c) Real plane image (b) and back focal plane image (c) of the plasmon emission with a SAM of SC₆ (n = 12) on a 50 nm AuTS film at a −1.8 V bias. (d) the defocused plasmon emission image of b [185].
tunneling. This observation was further confirmed by changing the tilt angle to ~10° by simply replacing the Au by a Ag bottom electrode. Using these junctions, plasmons could also be excited in plasmonic waveguides and bias-selective plasmon excitation was achieved with molecular diodes.

Noteworthy is that the plasmons are excited in discrete spots (Fig. 7b). It is well-known in electrical engineering that the current does not flow uniformly across most junctions and that the effective electrical contact area may be 2–4 orders of magnitude smaller than the geometrical contact area [186]. The effective electrical contact area in SAM-based junctions with EGAln top-electrodes was recently estimated to be 4 orders of magnitude smaller than the geometrical contact area [187,188]. The data shown in Fig. 7b shows visually that indeed the current flow across these junctions is highly inhomogeneous.

4. Molecular electronics applied in plasmon detection

The electrical detection of plasmons is the reverse process of plasmon excitation, and can also be classified as direct and indirect plasmon detection strategies as depicted in Fig. 8. Direct plasmon detection is realized by plasmon assisted tunneling. Indirect plasmon detection has two steps. Firstly, plasmons induce electron–hole pair generation. Secondly, these electron–hole pairs are separated and collected resulting in a photocurrent. Here, we review the direct plasmon detection based on the molecular tunnel junctions.

4.1. Mechanism of electrical detection of plasmons

Molecular tunnel junctions can be used to detect plasmons both indirectly and directly. Because of the plasmonic field, the average tunnel barrier height of the junctions is reduced and thus the tunnel current increases (Fig. 8a). This process is in-principle the photon-assisted tunneling (PAT) introduced by Tien and Gordon [189,190], however, because in plasmon detection the electromagnetic field is provided by plasmons, this effect can also be named as plasmon-assisted tunneling. In PAT, the plasmonic fields produce an electric field which can be approximated as an effective ac bias $V_{ac}\cos(\omega t)$ added to the applied dc bias where $V_{ac}$ is the ac bias amplitude, $\omega$ is the frequency of the plasmon and t is time. This ac bias then modulates the dc tunnel current given by Refs. [85,189,190].

$$I_{dc+ac}(V_{dc} + V_{ac}\cos(\omega t)) = \sum_{n=-\infty}^{\infty} i_{dc}(n\hbar\omega/e)\frac{V_{dc} + n\hbar\omega}{e}$$

where $\hbar$ is the reduced Planck’s constant and $e$ is the elementary charge. The increased current $\Delta I_{dc}$ due to the ac bias in the limit of small ac amplitudes ($eV_{ac}/\hbar\omega$) can be approximated by

$$\Delta I_{dc} = \frac{1}{4}V_{ac}^{2}
\left(\frac{\hbar\omega}{e}\frac{V_{dc}}{\hbar\omega} + \frac{V_{dc} - \hbar\omega/e}{2}\right)$$

(3)

If the variation of the tunneling current is small on the bias scale of $\hbar\omega/e$, Eq. (3) can be simplified to [85]

$$\Delta I_{dc} = \frac{1}{4}V_{ac}^{2}
\left(\frac{\hbar\omega}{e}\frac{V_{dc}}{\hbar\omega} \right)$$

(4)

On the contrary, indirect plasmon detection with molecular tunnel junctions utilizes electronically decoupled molecules with a smaller bandgap (e.g., conjugated molecules, Fig. 1d) as the tunneling barrier. Similar to photon detection using semiconductors, when plasmonic electromagnetic fields reach the tunnel junctions, the molecules will absorb the plasmon energy and generate electron–hole pairs which are then separated in an applied electric field resulting in a photocurrent (Fig. 8b). To realize effective indirect plasmon detection using molecules, there are fundamental issues to overcome. Firstly, the intrinsic HOMO–LUMO gap of the molecule limits the detection bandwidth. Secondly, the electron–hole generation is usually on the time-scale of nanoseconds which limits the response speed. So far, indirect plasmon detection has mainly been investigated based on miniaturized semiconductors connected to plasmonic waveguides in forms of Au films [191], single crystalline Ag nanowires [192,194,198], polycrystalline Au waveguides [195–197], and MIM gap plasmon waveguides [193].

4.2. Direct plasmon detection with molecular tunnel junctions

Direct plasmon detection with molecular tunnel junctions has been realized using molecules with large HOMO–LUMO gaps (e.g., aliphatic molecules, Fig. 1e) as the tunnel barrier using junctions of the form of Au NW–SAM–Au (NW = nanowire) sandwich by Noy et al. [199,200]. Fig. 9a shows the suspend nanowire molecular tunnel junctions with SAMs of SC$_6$ with n = 8, 10, 12. SPPs were excited using a laser and propagated along the Au NW to the junctions. The SPPs caused an increase in the observed dc tunneling current (Fig. 9b). The inset of Fig. 9b shows a fit of Eq. (4) to a plot of the increase in the dc current as a function of $V_{app}$ and the authors concluded that PAT explains their observations well. From the magnitude of the plasmon modulated current, it is also possible to determine the strengths of the plasmonic field in the junctions. The enhancement by the plasmonic fields should decay exponentially with the length of the molecule (i.e., the value of n). The authors found a plasmonic field enhancement of a factor of ~550 for n = 8, ~250 for n = 10, and ~100 for n = 12. Such an evolution of plasmonic field enhancement is normally difficult to measure directly by optical means because of the small dimensions of the gap (~1 nm). The direct plasmon detection of the molecular tunnel junction provides the opportunity to combine molecular electronics with plasmonics and in situ determination of plasmonic effects.

Direct plasmon detection has also been performed with junctions using continuous gold films as the electrodes. Fig. 9c shows squeezeable break junctions of the form of Au film–SAM–Au film [201]. These junctions support SPPs on their continuous gold films which can be excited with a p-polarized light in the Kretschmann configuration using a glass prism. When the thin gold films were squeezed to form a single molecule tunnel junction, SPPs were also squeezed in the junction area resulting in high local electro-
magnetic fields and significant increase of the observed tunneling current (Fig. 9d).

5. Conclusions and outlook

This Review highlights the great opportunities for molecular plasmonics by taking advantage of both the concepts of plasmonics and molecular electronics. Judiciously designed molecular tunnel junctions provide an interesting experimental platform to improve our understanding of quantum plasmonics (including charge transfer plasmons) and to demonstrate promising applications involving plasmonic resonances and detection. Although the feasibility of combining molecular electronics and plasmonics has been clearly demonstrated in the studies highlighted in this Review, several challenges remain in molecular electronic plasmonics.

Modeling quantum plasmon resonances in molecular tunnel junctions is challenging. Usually, quantum plasmon models use homogeneous effective dielectrics corrected by quantum tunneling as the tunnel barriers. In reality, the molecules inside the junctions are not static, but vibrate as a result of thermal or inelastic excitations [185, 202–205], causing for instance blinking phenomena. For a given junction, the current flow may not be uniformly distributed across the junction area and, in general, the shape of the tunneling barrier is disputed [27, 206, 207]. These uncertainties complicate the construction of realistic models. On the other hand, although quantum plasmon resonances have been demonstrated using molecule junctions, active molecular electronic control of these resonances have not been demonstrated yet.

Molecular electronic on-chip plasmon sources and detectors have been investigated with dc biases, but these are potentially very fast as they operated on the quantum tunneling time-scales. To realize ultra-fast plasmonic electronic circuitry, it is important to fabricate molecular tunneling junctions with small areas (e.g., <1 μm²) to ensure small capacitances and minimal RC delay times. Finally, experimental demonstration of simple molecular plasmonic electronic circuits is still lacking. One of the reasons is that reliable large-scale fabrication of molecular tunneling junctions is still challenging although recent progress has been made [208–210]. Despite these challenges we believe that molecular electronic plasmonics is an exciting playground for both theorists and experimentalists with promising applications in areas complimentary to traditional semiconductor based electronics.

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