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Tailored Surfaces/Assemblies for Molecular Plasmonics and Plasmonic Molecular Electronics

Jean-Christophe Lacroix, Pascal Martin, and Pierre-Camille Lacaze

Department of Chemistry, University of Paris Diderot, ITODYS, Paris 75205, France; email: lacroix@univ-paris-diderot.fr

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localized surface plasmon resonance, nanolithography, bottom-up methods, active plasmonic devices, hot carriers, charge transfer plasmon resonance

Abstract

Molecular plasmonics uses and explores molecule–plasmon interactions on metal nanostructures for spectroscopic, nanophotonic, and nanoelectronic devices. This review focuses on tailored surfaces/assemblies for molecular plasmonics and describes active molecular plasmonic devices in which functional molecules and polymers change their structural, electrical, and/or optical properties in response to external stimuli and that can dynamically tune the plasmonic properties. We also explore an emerging research field combining molecular plasmonics and molecular electronics.

1. INTRODUCTION

Surface plasmons were predicted long ago by Ritchie (1), but the use of plasmonic nanostructures for the confinement and manipulation of light in matter at the subwavelength scale is more recent. Its effective development dates from the beginning of the 2000s, when it appeared that photonic plasmonic devices could be made compatible with the miniaturization of the electronic circuitry at the nanoscale (2). From that discovery, two main topics were developed: One was devoted to the study of localized surface plasmon resonance (LSPR) in metal nanoparticles (NPs), and the other was focused on the propagation of surface plasmon polaritons (SPPs) in subwavelength waveguides confined at metal/dielectric interfaces.

Some metallic NPs exhibit coherent but confined oscillations of the quasi-free electrons in the conduction bands. When the characteristic frequency of these oscillations coincides with that of the light excitation, the response of the NPs becomes resonant, and strong absorption in the visible and near-infrared range occurs, called LSPR. Because of a strong exaltation of the electric field (3) that occurs very close to NP structures, localized surface plasmons (LSPs) have the capability of nanoantennas running at optical frequencies; they can also work as nanosensors (4), particularly adapted to the analysis of traces in the case of surface-enhanced Raman spectroscopy (SERS) (5, 6). One of the most promising characteristics of LSPR is that it occurs at frequencies corresponding to typical electronic excitations of molecules. This leads to the appearance of strong interactions between LSPs and molecular systems placed in the vicinity of metals, which allow one to manipulate the other and make it possible to develop active molecular plasmonic devices. The grafting of molecules onto plasmonic resonators also represents a new approach for studying the electronic properties of organic compounds, a new domain named plasmonic molecular electronics.

With SPPs, and in contrast to LSPs, the electromagnetic waves that are coupled to the coherent oscillation of free charge carriers in the metal propagate along the interface between a dielectric and a conductor (2, 7–9). The propagation length of SPPs depends on the metal and the incoming light wavelength. Even though resistive heating losses in metals can severely limit the performance of devices, many useful functionalities have been realized despite these losses [waveguides and nanoscopic light sources (7)]. The devices used are essentially chains of regularly spaced plasmonic nanostructures [nanoholes (7, 10), metallic nanoasperities or metal gratings (11, 12), metal grooves (13), NPs of various shapes (14–16), and nanowires (17–20)] or planar interfaces between a conductor and a dielectric (21). A new tendency has arisen involving the replacement of gold or silver by more common materials, such as doped metal oxides, semiconductors, or graphene (22). Because SPPs can localize and guide light over distances of several tens of microns in metallic structures (2), plasmonics offer a unique opportunity to merge photonics and electronics at the nanoscale (23, 24). This area constitutes a specific domain of research that strongly depends on the physics community; therefore, it will not be discussed in this review, which is devoted solely to the study of LSPR in interaction with molecular systems.

In the following sections, we describe the main techniques used for the fabrication of nanostructures leading to LSPR and the new properties resulting from the assembly of such structures with molecules. In particular, we discuss in more detail how the LSPR changes in active molecular plasmonic devices when grafted functional molecules and polymers are submitted to external stimuli that modify their structural, electrical, and/or optical properties. Another emerging research field combining molecular plasmonics and molecular electronics, in which hot carriers are produced, is also reviewed. Finally, we emphasize that this review is not exhaustive but is an attempt to provide a critical discussion of what we think is most important in this field, in the hope of communicating the opportunities and exciting aspects of the subject.

To control the LSPR frequency, the size and shape of the NPs, as well as their organization and spacing on the surfaces, need to be controlled. Fabrication of photonic nanostructures is dominated by top-down lithography techniques, but recent advances have used bottom-up assembly to construct large arrays of homogeneous nanopatterned surfaces and materials. Top-down approaches, such as lithography, those using electrons, photons, atoms, and ions, as well as embossing and scanning tip methods, offer high precision and resolution to the final structure of the plasmonic system. However, they are generally expensive and cannot create large-scale structures due to serial processing. In contrast, bottom-up approaches rely on the self-driven assembly of basic building blocks into ordered periodic structures and are generally faster and cheaper; they can also be used on a larger scale than top-down approaches. A formidable challenge that remains is to control the assembly and positioning of NPs at desired locations over large areas with high precision and high levels of integration. Of particular importance in recent research is the fabrication of plasmonic homo- or heterodimers consisting of two NPs separated by a nanometric gap. By filling the gap with various molecules, new molecular plasmonic devices can be achieved; we illustrate this trend in Section 4.2. Readers can find more examples of synthesis, nanomanipulation, and self-assembly of NPs in a recent review (25).

2. TAILORED SURFACES/ASSEMBLIES FOR MOLECULAR PLASMONICS

2.1. Top-Down Lithographic Fabrication

Electron beam lithography (EBL) (26) and focused ion beam (FIB) lithography (27) are among the main techniques used in the semiconductor industry for the fabrication of nanoelectronic devices. Whereas FIB lithography uses sputtering and etching to machine objects at the nanoscale, EBL is used to draw shapes on a surface covered by an electron-sensitive film called a resist. In traditional EBL, a focused electron beam is scanned over a thin resist layer and irradiates specific regions according to a programmed pattern (26). Poly(methyl methacrylate) is a common positive resist, which breaks down when exposed to the electron beam. After removal of the exposed regions with a solvent, metal can be deposited onto the substrate, usually by physical vapor deposition. EBL allows for precise control of the metal nanostructures, including the size, shape, and separation between them. It can generate a wide range of morphologies, including cylinders of various diameters and heights, dots, squares, and triangles (28-29). EBL resolution, depending on the nature of the resist, can reach the 2-nm feature size (26) in very specific experimental conditions, but the major drawback is that EBL is quite time consuming, and the costs associated with the equipment are high. Similar to EBL, a resist can be patterned by FIB lithography (27). However, FIB is used as a direct (i.e., maskless) physical patterning tool, through milling, as demonstrated for the formation of grooves (13), with Ga^+ ions used most frequently as the etching beam. The resolution is similar to that of EBL, and the drawbacks are the same. Another distinction is that FIB is capable of producing much deeper structures (with correspondingly high anisotropies) compared to EBL.

2.2. Bottom-Up Methods

The synthesis of colloid gold nanoparticles (AuNPs) of various shapes (spheres, nanorods, nanocubes, triangular or hexagonal plates) has been reviewed (25) and is not discussed here. These NPs are stabilized by capping agents that play a major role in their deposition. The simplest methods for immobilizing them on surfaces use electrostatic interactions (30). Various functional



(*a*) Model of Au–Ag@SiO₂ heterodimer deposited on a glass substrate and SEM images of two fabricated dimers. Adapted with permission from Reference 34. Copyright 2013 American Chemical Society. (*b*) SEM image of AuNPs fabricated by electrochemical deposition onto ITO substrate. Adapted with permission from Reference 39. Copyright 2016 IOPScience. (*c*) 2D hexagonal close-packed AuNPs generated using the self-assembly technique with thiol spacer. Adapted with permission from Reference 25. Copyright 2016 Royal Society of Chemistry. *d*) 2D arrays of PEG-AuNPs fabricated by the Langmuir-Blodgett technique from block copolymer. Adapted with permission from Reference 47. Copyright 2015 American Chemical Society. Abbreviations: 2D, two-dimensional; AuNP, gold nanoparticle; ITO, indium tin oxide; PEG, polyethylene glycol; SEM, scanning electron microscope.

binding groups, such as amino (31), thiolate (32), or siloxanyl (33), can be used to control these electrostatic interactions or to add chemisorption to the deposition process. The NPs stick to the surface but are generally not organized, and their densities and spacing cannot be controlled by these deposition methods.

Electrostatic assembly of plasmonic heterodimers, consisting of Ag@SiO₂@PAH [poly(allylamine hydrochloride)] and Au@PVP [poly(vinylpyrrolidone)] NPs, has been reported (34). Binding was achieved between a silver particle with a positively charged shell PAH and a weakly negatively charged AuNP coated with PVP. Interaction between the two different core–shell structures allows preassembly in solution, and the dimers were transferred to a substrate (**Figure 1***a*) by spin coating to study their LSPR.

Electrochemical deposition is a useful method for synthesizing and immobilizing AuNPs on substrates simultaneously (35–37). With this method, it is relatively easy to control particle morphology. Many studies reported various shapes of NPs: El-Deab et al. (37) worked on NPs having unique shapes, with bumpy, thorny, and dendritic morphology on carbon and gold electrodes. However, such substrates were not used as plasmonic devices. More recently, Nguyen et al. (38) used electrodeposition to generate large-area plasmonic AuNP arrays (up to several square centimeters) on indium tin oxide electrodes. These AuNP substrates (**Figure 1***b*) exhibit a strong, sharp LSPR signal, which compares well with those of gold arrays deposited by EBL (39), and

constitute low-cost plasmonic electrodes. However, the electrochemical reduction of gold salts does not allow for the control of NP spacing.

Several methods have been developed to enhance the control of periodicity or spacing between colloidal NPs deposited on surfaces. Colloidal NPs assembled at air/liquid/solid interfaces by dip coating, drop coating, or Langmuir-Blodgett (LB) techniques are widely used. The first two are crude methods developed for nanosphere lithography (NSL), whereas LB is a more sophisticated and advanced method for interfacial assembly that was initially used for organizing organic molecules into ordered structures (40). It has been extended to organize NPs into regular arrays on solid substrates at the centimeter scale (41). In the case of polystyrene or silica beads, the organized surfaces are used in a subsequent step as templates to generate a plasmonic substrate by NSL (see Section 2.3). With gold colloid NPs, well-organized plasmonic surfaces can be obtained directly (42). As an example, **Figure 1***c* shows two-dimensional (2D) hexagonal close-packed AuNPs deposited on quartz. Interparticle gap size can be controlled from 2.3 to 3.4 nm by coating the AuNPs with various alkanethiols, with chain lengths from 12 to 18 carbons. Good control of the LSPR wavelength from 607 to 575 nm was demonstrated (42, 43).

Block copolymers and polymers can also self-assemble on surfaces (44, 45). This property was recently used to create tailored plasmonic surfaces by preassembling NPs at the liquid/air interface before LB deposition. For example, a 2D network via a quasi-one-dimensional (1D) arrangement of silver clusters in the PVP matrix was formed at an aqueous interface, and subsequently, these NP assemblies were transferred onto a substrate (46). Similarly, close-packed hexagonal structures (**Figure 1***d*) of AuNPs of different sizes, separated by a length of block copolymer, exhibit well-defined LSPR (45, 47). This strategy was also recently used on an HfO₂ substrate (48).

Another trend consists of using self-assembled prepatterned surfaces to deposit NPs selectively with controlled alignment, size, and shape (49). Ohtani and coworkers (50) investigated the fabrication of well-aligned necklace-like assemblies of AuNPs using stretched strands of DNA as a template (51, 52).

Several examples have been described of a topographic structure defined by lithography being used to trap NPs in defined positions (53, 54). The spatial confinement parameters (height, width, and length of the template) play an important role in the organization of NPs. The template size has to be commensurate with the particle size. Therefore, the arrangement of sub-30-nm NPs remains difficult due to the resolution limit of lithographic techniques. However, this limit can be overcome by changing the ionic strength in the solution to modulate the thickness of the electric double layer that must be added to the radius of the NPs to give their effective radius. Using this principle, Chi and colleagues (55) created 1D single-particle chains with small particles (13 or 32 nm) and on surfaces with large nanostructured (70 or 160 nm) grooves. They also designed a nanostructured surface to fabricate multiplexed 1D NP arrays with different particle sizes (Figure 2b) (56). Plasmonic devices with fine control of interparticle spacing were fabricated in the same way (57). Changing the concentration of NaCl solution generated well-ordered 2D arrays of AuNPs and AgNPs on an amino-modified surface. These examples clearly show that the combination of top-down approaches and electrostatic assembly of NPs is a powerful way of fabricating reproducible, well-ordered 1D or 2D periodic arrays of NPs at desired locations on a single chip.

2.3. Nanosphere Lithography

Developed by Deckman and Dunsmuir in 1982, NSL is an inexpensive and versatile bottom-up procedure for fabricating periodic and large-area arrays of metallic structures on substrates (58–61). In general, NSL involves the preparation of a well-ordered template, based on a hexagonal



(*a*) SEM image of 2D colloidal "soap"-gels (stearic acid/octadecylamine/AuNPs) deposited on a silicon wafer using the Langmuir-Blodgett technique. Adapted with permission from Reference 165. Copyright 2012 American Chemical Society. (*b*) AFM topographies of 1D arrays of 32-nm AuNPs site-selectively self-assembled in the broader grooves (160 nm) but not in the narrower ones (100 nm) nearby. Adapted with permission from Reference 49. Copyright 2014 American Chemical Society. (*c*) Ternary surface pattern created by combining the masking and scaffolding modalities of colloidal templates. Left: large-scale organization. Right: Magnified view of the ternary pattern. Adapted with permission from Reference 64. Copyright 2014 American Chemical Society. (*d*) SEM images of uniform 2D hexagonal close-packing lattices of nanoholes with different hole diameters and lattice periods. Adapted with permission from Reference 166. Copyright 2007 IOPScience. Abbreviations: 1D, one-dimensional; 2D, two-dimensional; AFM, atomic force microscopy; AuNP, gold nanoparticle; ITO, indium tin oxide; PEG, polyethylene glycol; SEM, scanning electron microscope.

close-packed layer of monodisperse particles on a substrate, and yields defect-free domains approximately 10 μ m² to 1 cm² in area. This hexagonal arrangement contains free spaces between three neighboring particles and can be used as a mask for deposition or etching. E-beam evaporation (62–64), electrodeposition (65, 66), or magnetron sputtering (67) is then used to deposit metal or other materials through the mask. In the case of vapor phase deposition, normal or different angle incidence can be used during the deposition step to generate interesting nanostructures. Nanotriangles, nanopyramids, nanorings, or inverted nanocones can be generated by varying the particle size or the treatment of the hexagonal template (59). This technique makes it possible to tailor precisely the plasmonic substrate by generating complex systems. For example, Yang et al. (64) describe the fabrication of binary and ternary structures by combining two processes (e.g., scaffolding and masking) of a nanosphere monolayer (**Figure 2***c*). Plasmonic coupling gives rise to a strong LSPR peak in the near infrared (~1,200 nm) due to the higher spatial density of NPs of binary patterns. In this case, plasmonic properties are highly dependent on the size and spacing

of the core and satellite AuNPs in the complex patterns. It opens a way for new architectures for tailored plasmonic surfaces working in the near infrared.

An etching step (oxygen plasma) was used by Vogel et al. (68) to transform a close-packed monolayer of beads into a nonclose-packed monolayer. This process allows the formation of other nanostructures, such as nanodisks (69, 70) or nanowells (71). Using a similar strategy, Walter et al. (70) investigated the fabrication of heteromaterial nanodisks for a low-cost plasmonic absorber device. Au/MgF₂/Au nanodisks were fabricated by combining NSL, etching, and heteromaterial substrates. The absorption of the heterostructure device remains extremely high at all polarizations, and the wavelength can be tuned from 800 to 1,000 nm.

Nanospheres as a lithography mask working as a nanolens were used to prepare 1D or 2D nanoholes (**Figure 2d**) (72, 73), allowing the fabrication of dimer plasmonic devices (74, 75). Many examples have been developed with the simple or sophisticated NSL technique, showing the versatility of this lithographic process and the great possibilities for the fabrication of complex and specific tailored plasmonic surfaces.

3. ACTIVE MOLECULAR PLASMONIC DEVICES

The LSPR frequency depends mainly on the size, shape, and spacing of the particle and on the dielectric constants of the substrate and surrounding medium. Thus, the LSPR can be reversibly controlled by tuning these different parameters with an external stimulus. Of particular interest are systems in which the input is linked to functionalized molecules deposited on, or in the vicinity of, the plasmonic structure. By controlling some parameters of the molecule, it is possible to modify the spacing of the NPs, the apparent dielectric function of the surrounding medium, and/or the electromagnetic coupling between the plasmon and the molecule. This control can be achieved by chemical, electrochemical, electrical, optical, mechanical, and thermal inputs, and allows the development of a wide variety of active molecular plasmonic devices.

LSPR modulation is widely used to design sensors and biosensors (4–6, 76). Even though such devices can be considered as active plasmonic devices, their purpose is not to control the LSPR but to use it as a transduction of the molecular events occurring at the NP surface. The large body of research on plasmon-based sensors is not discussed here. Let us just add that the LSPR of isolated NPs shows limited sensitivity to recognition events. However, LSPRs are highly sensitive to interparticle spacing, originating from the near-field plasmon coupling of NPs. In particular, particle aggregation results in a pronounced red shift of the LSPR, and most of the applications for sensors, including recently developed plasmon rulers for biology (77), are based on this distance variation.

Electrochemistry on nanostructured electrodes supporting LSPR allowed the development of the first active molecular plasmonic devices. Sweeping or changing the potential of a plasmonic electrode in an electrolyte yields small LSPR wavelength shifts (10 nm/V) in the potential regime dominated by double-layer charging (78, 79). Deposition on the NPs of an electroactive monolayer or thin film makes it possible to trigger LSPR using the oxidoreduction properties of the deposited layer by the potential applied to the electrode. Wang & Chumanov (80) were the first to use this strategy. They deposited a thin film of tungsten oxide WO₃ on AgNPs. By switching the applied potential between 0.6 and -1 V, the optical extinction signal was reversibly modulated, and a 40-nm blue shift was observed. Following that, we reported the use of electroactive conductive polymer (CP) thin layers deposited on gold gratings (31, 81). In a first study, a large blue shift of the LSPR from 633 to 571 nm, accompanied by a strong damping, occurred when a 100-nm–thick polyaniline (PANI) film was reversibly switched from its reduced state to its oxidized state. In a second step, we showed that the LSPR in such a PANI/AuNP hybrid material exhibits



(*a*) Extinction spectra of prolate gold particle grating (X-polarized light) in air (*black curve*), overcoated with a PEDOT/SDS film in its oxidized state (*blue curve*), and overcoated with a PEDOT/SDS film in its reduced state (*red curve*). Adapted with permission from Reference 85. Copyright 2010 American Chemical Society. (*b*) Two types of coupling behaviors between a plasmon and a molecular chromophore: plasmonic splitting (*red curve*), energy transfer (*green curve*) and uncoated (*black curve*). Adapted with permission from Reference 127. Copyright 2012 American Chemical Society. Abbreviations: LSPR, localized surface plasmon resonance; SDS, sodium dodecyl sulfate.

progressive damping as a function of the applied potential and that the observed modulations are closely related to the charge-carrier density injected into the CP (82). Anisotropic responses were also observed using prolate NPs covered with PANI (83).

Several groups have investigated the effect of switching other CPs on the LSPR of AuNPs (84, 85). Indeed, the variation of the dielectric constant depends greatly on the nature of the CP, and changing it modifies the optical response of the device to switching. For example, a plasmonic substrate consisting of highly ordered 2D arrays generated using the LB technique and covered by polythiophene films exhibits a reversible blue shift of 9 nm upon switching the CP (47). We also reported the variation of the LSPR of AuNP arrays covered with PEDOT/sodium dodecyl sulfate as a function of the electronic state of the polymer (85). The overall shift between reduced and oxidized states was 192 nm (**Figure 3***a*). This giant plasmon resonance shift, covering almost half of the visible spectrum, is unique to the best of our knowledge. This shift, attributed to the variation of the PEDOT dielectric function upon doping, is also partially enhanced by a strong overlap between the LSPR and the PEDOT absorptions, which results in strong optical coupling between the NPs and the CP. These results, useful for the design of active plasmonic devices, are also interesting for CP-based electrochromic systems, because new colors, electrochromic contrast, and color efficiency could be obtained by using various combinations of an AuNP array and a CP.

Such a direction was developed with gold nanorods combined with a solution-processable electrochromic/electroactive CP, an alkoxy-substituted poly(3,4-propylenedioxythiophene). Large, stable, and reversible LSPR modulation of 25–30 nm was obtained (86). Gold nanocubes (AuNCs) coated with electrochromic PANI shells were also reported (87). The LSPR peak of the AuNC core was reversibly tuned by applying an electrical potential that caused a reversible oxidation state change in the PANI nanoshell. In another study, a single gold nanorod core/PANI shell nanostructure displayed remarkable switching behavior, with modulation depth and scattering peak shift reaching 10 dB and 100 nm, respectively (88).

We recently used ultrathin oligothiophene layers grafted by diazonium electroreduction onto AuNPs (89) and compared systems based on physisorbed electroactive layers (weak electronic coupling) with those based on covalently bonded layers (strong electronic coupling). In both cases, redox switching of the electroactive layer tunes the LSPR of the AuNPs. However, the amplitude of the LSPR modulation depends on the electronic coupling regime between the NPs and the organic layer, suggesting that, in a strong electronic coupling regime, plasmon delocalization within the covalently grafted material is enhanced. Layer thickness also affects LSPR shift, with a minimal thickness of 30 nm required to achieve a large shift. This remains a drawback and constitutes a severe limitation of molecular active plasmonic devices using surfaces in which the individual NPs interact through far-field coupling.

Electroactive molecular machines grafted on NPs have also been used. A gold nanodisk array coated with bistable, redox-controllable [2]rotaxane molecules undergoes reversible switching of its LSPR when exposed to chemical oxidants and reductants (90). Nevertheless, it is noteworthy that the shifts were rather small (10 nm) because of the thinness of the monolayer.

The use of electrochemical switching and combining CP or electroactive molecules with plasmonic devices (e.g., nanoscopic light sources, waveguides) is a general means of controlling their properties. For example, surface plasmon resonance (SPR)-enhanced optical transmission was actively controlled by electrochemical switching of PANI and PEDOT (91). High-contrast electrochromic switching was also demonstrated with arrays of metallic nanoslits, whose sidewalls were coated with ultrathin PANI and PEDOT films (92). By controlling the pitch of the nanoslit arrays, it is possible to achieve a full-color response with high contrast and fast switching. Active modulation of the plasmon coupling in homodimers of PANI-coated Au nanospheres was also achieved by changing the proton-doping state of the PANI shell (93). This changes the near-field plasmon dimer coupling and gives rise to remarkable spectral shifts, which show exponential dependence on the interparticle gap distance. For the dimer with a 10-nm–thick PANI shell and a 0.5-nm gap, the shift of the stronger scattering peak in response to the conductance switch reaches 231 nm. Finally, the first example of triple coupling involving electrochemistry, fluorescence, and plasmon resonance, through the investigation of the electrofluorochromic properties of a tetrazine derivative on gold plasmonic working electrode gratings, was reported (94).

Another input for controlling LSPR is the application of an external electric field. It is especially significant because both plasmonic and electric signals can be guided in the same metallic circuitry. The effects of integrating liquid crystals (LCs) with AuNPs (95), gold nanodots (96), gold nanorods (97, 98), and nanohole arrays (99) were investigated. In all cases, the SPR depends on the applied voltage. As an example, a strong modulation of the LSPR intensities of individual gold nanorods with applied voltage as low as 4 V was reported (100). Berthelot et al. (101) used an LC as a load for filling the gap between a single-dimer optical antenna. They demonstrated that the strength of the interaction between the two metallic NPs forming the dimer antenna can be controlled by an electrical input that affects the alignment of the in-plane orientation of the LC molecules. Another study used plasmonic clusters supporting Fano resonances (102). When this structure was incorporated into an LC device geometry, the entire Fano resonance spectrum was switched on and off by applying a voltage. A reversible transition between the Fano-like and non-Fano-like spectra was induced by relatively low (6 V) applied voltages. Gold nanorods with a shell of nonlinear optical materials (such as PANI) with variable thickness were also developed. The formation of a PANI nanoshell allowed dynamic modulation of the dielectric environment of plasmonic gold nanorods and the plasmonic resonance characteristics by an external electrical field (103). The authors propose this system for a new generation of nanoscale optical voltage sensors.

Active modulation of LSPR by applying an electric field to AuNPs embedded in ferroelectric (zirconate titanate) films was also reported (104). Reversible LSPR shifts from 615 to 649 nm were observed when no field and a 500 kV/cm-field were applied. More recently, polyvinylidene fluoride was used to generate a system that can be stretched when an electric field is applied.

Sputtering silver nanoclusters on such a surface generated an active plasmonic device in which complete quenching of plasmon was electrically driven as a result of the induced mechanical stretch (105). Other plasmonic devices based on mechanical movement were reported (106).

Efficient methods to achieve optically driven plasmonic devices have been developed. Lightdriven plasmonic devices have several potential advantages: They could operate faster, light can be used for inducing (writing) as well as detecting (reading) the behavior of plasmonic devices, and they can be integrated in future all-optical plasmonic circuits. Optical control of SPP has been widely developed but rarely uses molecules. On the contrary, there are a number of reports on photosensitive AuNPs whose surface is coated with small molecules bearing a photochromic moiety. In the case of colloidal metallic NPs, azobenzene trans-cis photoisomerization was used to induce NP aggregation, resulting in the change of the interparticle distance and a shift of the SPR (107-112). Isomerization yields and switching speeds in such devices remain clear limitations, even though lowering the surface coverage of azobenzene provided more free space for isomerization to take place and enhanced the LSPR shift. Another example uses the optical switch of azobenzene side groups grafted on a copolymer of N,N-dimethylacrylamide and N-[4-(phenylazo)phenyl] acrylamide (108). LSPR switching via interaction with a chalcogenide phase-change material (GeSbTe) was reported. Upon irradiation with a femtosecond pulsed laser for amorphization and a continuous wave laser for crystallization, significant switching of the LSPR band was observed (113, 114).

Thermoresponsive layers surrounding NPs were also used to design thermally driven active plasmonic devices. Several groups have developed systems based on the thermally induced and reversible collapse of poly(*N*-isopropylacrylamide), pNIPAM (115–118). Changes in the spacing between the NPs induced by collapse of the polymer network led to a reversible red shift ($\Delta \lambda = 31$ nm) of the LSPR of gold nanorods. Similar modulation on lithographic AuNPs functionalized by pNIPAM was demonstrated. Optical modifications result from local refractive index changes due to the phase transition from a hydrophilic state (swollen regime) to the hydrophobic state (collapsed regime) of the polymer chains occurring in a very small range of temperatures (119). Other thermoresponsive plasmonic devices have been developed using LCs (120, 121). They confirm that the LSPRs in anisotropic media depend markedly on the local ordering of the media. Thin films of an iron^(II)-triazole–type spin-crossover complex coated on lithographically patterned gold nanorod arrays were investigated upon heating/cooling and also under 633-nm laser irradiation (122). In both cases, a reversible shift of the LSPR wavelength was observed and quantitatively related to the refractive index change accompanying the spin transition.

In most of the previous examples, the molecules used did not absorb light near the nanoantenna extinction. New phenomena occur when LSPR and molecular absorption coincide. Using AuNPs coated with the J-aggregate of an anionic cyanine dye, Kometani et al. (123) evidenced that the absorption spectrum of the dye-coated AuNPs was not a simple sum of the AuNP and dye contributions. It was characterized by an absorption dip at the position corresponding to the J-band of the dye (124). Van Duyne and coworkers (125) explored LSPR experimentally near molecular resonances. When the peak position of the NPs' LSPR is close to but above the molecular resonance, a large red shift is observed upon monolayer deposition, whereas the shift drops sharply when the initial LSPR exactly matches the molecular resonance. The influence of molecular adsorbates on the absorption spectra of spherical NPs was also investigated using arbitrary coupling to the surface and changing the molecular excitation characteristics through its HOMO–LUMO gap (126). Results showed that strong coupling can induce splitting of the resonance into two different excitations. The higher-energy broad peak was predicted to be located at the particle surface. The lower-energy excitation is located over the adsorbates and is attributed to an in-phase oscillation of molecular dipoles on opposite sides of the NP. This new excitation is similar to a

completely symmetric molecular exciton, in which molecular dipole oscillations couple in-phase. The oscillator strength of this excitation is several orders of magnitude higher than that of the bare molecule excitation due to the large distances involved. Another study (127) showed that two types of coupling behaviors, plasmonic splitting and energy transfer, which are manifested in experiments as peak splitting and a quenching dip, can be unified (**Figure 3***b*). However, three regimes attributed to enhanced absorption, exciton-induced transparency, and strong coupling were identified depending on the nature of the observed spectra of the coupled plasmon–exciton resonances (128).

Excitons and plasmons are the two main excited states of matter; thus, understanding their interactions is an important research field. Strategies based on tuning the strength of the coupling through some physical or chemical input have been reported and considerably widen the opportunities to achieve active molecular plasmonic devices (129–131). They should demonstrate extreme sensitivity over a large spectral range, as addressing one of the hybrid resonances could both affect coupled resonances and alter the extinction of the device over a large spectral range (131). Strong coupling of chromophore and plasmon resonances has been exploited for molecular sensors (124, 132, 133). Other examples of this activity can be found in two recent reviews (134, 135). Research recently demonstrated strong coupling between plasmons confined within a single silver nanoprism and excitons in molecular J-aggregates under ambient conditions (136).

4. PLASMONIC MOLECULAR ELECTRONICS

It is now well recognized that the use of plasmonic nanostructures in interaction with adsorbed molecular compounds constitutes a new pathway to drive photocatalysis and improve the efficiency of a chemical reaction where hot carriers appear prominent (137, 138). Recently, their action was also shown to improve the efficiency of photovoltaic (139, 140) and electroluminescent devices (141, 142). The ways in which hot carriers are involved in a chemical process are still under debate and depend on their energy characteristics, their distribution, and how the physical contact between the nanostructure and the adsorbate is established. In the following sections, we discuss these different points and also show how the grafting of molecules on plasmonic resonators is a new approach for studying the electronic properties of organic compounds, a new domain designated as molecular electronic plasmonics (143). However, it is valuable to recall some fundamental results obtained with plasmonic nanostructures without molecular compounds.

4.1. Plasmonic Coupling Between Two Metallic Nanoparticles

One of the most frequently used systems is that of a plasmon dimer wherein two NPs are separated by a nanometer or subnanometer vacuum gap. This system was investigated by several groups (144–147) and later revisited by Zuloaga et al. (148).

The plasmon absorption spectra of NP dimers depend on the separation distance, *d*. When it is greater than 0.25 nm, the interaction is mainly dipolar and can be calculated classically from the Maxwell equations. The photonic excitation of the nanostructure gives rise to an intense electromagnetic field located between the NPs, and the scattered light steadily red shifts when *d* decreases from 1.25 to 0.25 nm.

For subnanometer separations of the NPs (0.25 nm $\ge d \ge 0$), when the two NPs are separated by a distance where tunneling in vacuum between two electrodes becomes dominant, a new plasmonic mode, called the charge transfer plasmon (CTP), appears; this results from electron transfer tunneling between the NPs. This oscillation frequency blue shifts when the gap decreases, contrary to the case of the dipolar interaction, which red shifts.



(*a*) Left: Calculated scattered efficiencies of plasmonic dimers ①, ②, and ③. Diameter of the disc is 95 nm; width, length, and thickness of the bridge are 15, 30, and 35 nm, respectively. Right: Charge distributions corresponding to ①, ②, and ③, with (*i*) a dipolar plasmon for the nanorod, capacitively coupled BDP resonance, and (*ii*) a CTP resonance for the nanowire-bridged dimer and a BDP resonance for the dimer. (*b*) Left: Experimental dark-field scattering of nanowire-bridged Au dimers for various bridge widths (15–60 nm). Right: SEM images of the nanowire-bridged dimer. Adapted from Reference 149. Copyright 2015 American Chemical Society. Abbreviations: BDP, bonding dipolar dimer plasmon; CTP, charge transfer plasmon; SEM, scanning electron microscopy.

Another system consisting of two nanodisks connected by a metallic bridge was investigated (149). This model is interesting because it allows correlation of the plasmonic resonance of the system with the conductance of the bridge and prefigures what can be expected with a molecular junction.

Figure 4 depicts the three defined states of association of the two nanodisks: **1** is a nanorod resulting from the overlap of the two disks; **2** is a nanowire-bridged dimer; and **3** is a single dimer without a bridge (149). In the case of an electric field oriented along the axis of the dimer, **2** exhibits two plasmon resonances: one (i) matches the dipole resonance [bonding dipolar dimer plasmon, (BDP)], and the other (ii) is lower energy and corresponds to the CTP resonance (**Figure 4***a*). Then, by using metal bridges of greater width and thus of higher conductance, the authors show that both the BDP and CTP resonance is strong and very wide, whereas the dipolar resonance is very low and has blue shifted to 2.2 eV, further than the BDP resonance of the single dimer at 1.95 eV.

In conclusion, two NPs connected by a conducting bridge have BDP and CTP resonances that blue shift when the conductance of the bridge increases. This blue shift is attributed to a decrease in the electron transit time and therefore to an increase in the oscillation frequency of the electrons between the NPs. Note that the damping of the BDP resonance, from a bridge width of 20–30 nm, is dramatic, whereas the CTP grows stronger when the bridge conductivity increases.

4.2. Plasmonic Coupling Between Two Nanoparticles Bridged by Molecules

This system is very similar to the one described above and also allows us to probe cases where the molecular bridge can range from nanometer to subnanometer lengths. Therefore, it should allow researchers to distinguish between CTP and BDP modes, i.e., between a quantum mechanical tunneling regime and dipolar coupling.

The interaction between the plasmons generated in the nanostructure and the grafted molecules that bridge the NPs is usually studied in two experimental setups: (a) illumination of the nanostructure that induces a quantum plasmon resonance whose frequency depends on the electronic properties of the adsorbate, and (b) an applied bias voltage between the NPs that induces both a tunnel current through the junction and an emission of photons, whose intensities are also a function of the electronic properties of the molecules. Finally, when the nanostructure is illuminated under a bias voltage, the tunneling current is increased and also reflects the properties of the molecules. In each case, it must be emphasized that the plasmon resonance is accompanied by an emission of hot charge carriers that also interact with the adsorbed molecules and induce an additional damping of the plasmon resonance.

4.2.1. Molecular plasmonics in the quantum regime in molecular-bridged nanoparticles.

It was previously shown that irradiation of metallic NP dimers connected by a metallic bridge of variable conductivity could evolve from a BDP to a CTP regime involving tunneling charge transfer when the conductance of the bridge was increased. Similar effects are observed when the NPs are bridged by conjugated or nonconjugated molecules with different chain lengths. This approach allows us to modulate the energy barriers resulting from the contact between the metallic NPs and the molecular junction, therefore constituting another way of decreasing or increasing the conductance of the junction.

One of the first systems consists of self-assembled AuNP dimers or NP arrays obtained by bridging the gold nanostructures with dithiolated aliphatic hydrocarbons, $HS(CH_2)_nSH$, (n = 2–10), well known for their strong chemisorption on gold (150). The transition between the BDP and CTP modes was clearly observed (151).

Two plasmon resonance peaks are observed: (*a*) one at approximately 520 nm, whose intensity and position remain roughly constant when the chain length changes, is due to the transverse coupling of the surface plasmon with light; and (*b*) one centered between 600 and 650 nm involves the longitudinal coupling of light with the dimer. This latter peak red shifts when the chain (C) length decreases from C10 (10 CH₂, 1.6 nm) to C5 (5CH₂, 1 nm) and then blue shifts from C5 to C3, clearly demonstrating the transition from the dipolar regime to the CTP regime when the distance falls below 1 nm.

A similar study was carried out by Benz et al. (152) with AuNPs separated from a planar gold film by self-assembled molecular monolayers of two geometrically similar conjugated molecules, biphenyl-4-thiol (BPT) and biphenyl-4,4'-dithiol (BPDT) (**Figure 5***a*). Because of the different numbers of sulfhydryl groups, BPDT provides better contact than BPT (153). This difference between the two junctions appears in the SPRs, where a blue shift of the scattered light with BPDT (**Figure 5***b*) confirms that the CTP regime is effective.

Other experiments were performed with molecular junctions made of molecules of the same geometric length but differing in conjugation. Tan et al. (154) used Ag nanocube dimers excited by an electron beam and linked together either by 1,2-ethanedithiolate or by 1,4-benzenedithiolate (BDT). These molecules have approximately the same length but differ in their band gaps and therefore generate different junction barrier heights. Measurement of the electron energy loss shows that the CTP resonance only appears for the aromatic compound, BDT, which again confirms that this resonance can occur with lower energy barrier junctions.



Plasmon resonance with conjugated molecules. (*a*) Scheme of the plasmonic nanostructure obtained with BPDT bridging the gap between an AuNP and Au plate through two sulfhydryl groups. (*b*) Normalized scattered intensity of various individual AuNPs with BPDT and BPT spacers. Adapted from Reference 152. Copyright 2015 American Chemical Society. Abbreviations: AuNP, gold nanoparticle; BPDT, biphenyl-4,4'-dithiol; BPT, biphenyl-4-thiol.

4.2.2. Plasmon-assisted tunneling in polarized molecular nanostructures. Polarized plasmonic molecular nanostructures are usually discussed in the context of a scanning tunneling microscope (STM) gold tip above a gold plate and connected to it through a molecular junction (155). When a bias voltage is applied between the tip and the substrate through the molecular junction, light scattering occurs in the tip-substrate cavity. The origin of this emission is not obvious. It may be due to cavity plasmon resonance (156), the luminescence of the molecule induced by inelastic tunneling of hot electrons, or both.

The luminescence of molecules attached to a solid substrate and probed with an STM tip was discovered in the 1990s with fullerenes (157). The mechanism is now well established as being due to a plasmonic tunneling charge transfer, resulting from the production of hot carriers. Among several recent experiments, one involving a rigid molecule with a porphyrin fluorophore nucleus, perpendicularly adsorbed on Au (109) through an insulating tripodal anchor (158), illustrates this phenomenon well (**Figure 6**).

This molecular assembly provides self-decoupling of the molecule with the substrate (necessary to avoid the quenching of the luminescence) and the fixed orientation of the molecular vibrational dipole, which are both believed to favor the luminescence of the porphyrin nucleus. The bias voltage applied between the substrate and the tip generates the plasmon resonance of the nanocavity labeled NCP (nanocavity plasmon) in **Figure 6***c* and is accompanied by the production of hot electrons. These electrons are transferred by tunneling into the lowest unoccupied molecular orbital (LUMO) of the molecule. Electroluminescence could occur through the excited state relaxation of the molecule, but it requires a simultaneous flow of electrons toward the substrate. This is possible if the highest occupied molecular orbital (HOMO) is aligned with the Fermi level of the substrate. Precisely, this occurs when a positive bias with an onset of approximately +1.9 V is applied between the substrate and the tip. A negative bias (-2.5 V) does not produce electroluminescence. The origin of such unipolar performances is still not completely clear and



(a) Molecular fluorophore assembly perpendicularly adsorbed on Au at a base pressure of 8×10^{-11} mbar at 80 K. (b) Energy diagram compatible with plasmon-induced fluorescence resulting from the tunneling of hot electrons. (c) Fluorescence emission versus bias voltage clearly shows that a negative bias or an overly low positive bias prevents electron tunneling and is therefore unsuccessful in producing light emission. Adapted from Reference 158. Copyright 2013 American Chemical Society. Abbreviations: E_F^S , Fermi level of the substrate; E_F^T , Fermi level of the tip; E_{HOMO} , energy level of the highest occupied molecular orbital; E_{LUMO} , energy level of the lowest occupied molecular orbital; NCP, nanocavity plasmon; STML, scanning tunneling microscope luminescence; Vac, vacuum; V_b , bias voltage between substrate and tip.

depends on the energy level alignment and coupling at the interfaces. As claimed by Zhu et al. (158), this assembly could be of interest in the development of nanoscale light emission diodes.

The production of hot charge carriers (recently reviewed in 159) from plasmonic nanostructures is indeed very important, but the way they interact with adsorbates remains unclear and needs to be better understood to improve their efficiency in photocatalysis, where plasmonic nanostructures are involved. The usual method of production consists of illuminating a plasmonic nanostructure at LSPR frequency. A second but less common way is to apply a bias voltage in a nanocavity consisting of two plasmonic nanostructures placed very close to each other, as previously described with the STM setup.

In the conventional mechanism (**Figure** 7*a*), excitation of an electron-hole pair is extremely rapid, occurring in approximately 1 fs, after which relaxation and return to the thermal equilibrium occur within approximately 1 ps. Electron transfer from the metal to the adsorbate [known as interface damping (160)] can theoretically take place at any moment during the thermalization process but with a low probability due to rapid cooling. Another path is possible when the adsorbate interacts strongly with the NPs (**Figure** 7*b*). The strong field near the surface facilitates electron-hole pair formation (hot spots have field intensities 10^4 – 10^5 times higher than those of the incident light). Direct electron transfer toward unpopulated adsorbed states can then bypass the electron thermalization process and therefore substantially increase the catalytic activity of the plasmons.

Such improvements were recently demonstrated by Wu et al. (161, 162) with the tailoring of CdSe–Au heteronanostructures composed of a semiconducting CdSe nanorod (average length: \approx 26 nm, radius: \approx 3.6 nm) having at its end an AuNP (radius: \approx 5.4 nm). In this case, the relaxation of electron–hole pairs in the metal is considerably decreased, thereby increasing the transfer efficiency of hot electrons to the semiconductor. Recently, Liu et al. (140) showed that the use of Ag platelets firmly adsorbed on structured n-Si nanowires significantly increases the efficiency of hybrid photovoltaic cells (ITO/PEDOT:PSS/n-Si/Al-Ag). Compared to a simple hybrid cell



(a,b) Resonant charge transfer following a plasmon decay according to a (a) conventional or (b) direct mechanism. The drawings represent the density of states versus energy in the nanoparticles and adsorbates. Populated states are in blue, unpopulated states in white. Adapted from Reference 164. Copyright 2016 American Chemical Society. (c,d) Raman spectra of methylene blue adsorbed on Ag nanoparticles for two excitation wavelengths (785 and 532 nm) indicating the (c) transfer of hot electrons or (d) lack thereof. Adapted from Reference 163. Copyright 2016 Nature Publishing Group.

(without platelets), the photocurrent density and power efficiency increase by approximately 28% and 40%, respectively. The Ag platelets absorb light from the visible to the near infrared (550–1,100 nm), and the improvement in the conversion efficiency is attributed to the hot electrons they generate. Recent papers from Linic's group (163, 164) are particularly significant and provide new experimental data that shed light on plasmon-mediated photocatalytic processes. They demonstrate that a direct transfer from plasmonic excitation toward an excited state of the NP-adsorbed molecule system is made effective when the molecule and the plasmonic NP are firmly intricated and constitute a kind of molecular hybrid.

This direct charge transfer was evidenced for methylene blue chemisorbed on AgNPs. The demonstration is based on the idea that direct charge transfer fills upper vibrational states of the molecule and thus leads to a vibrationally excited state. This excited state can be detected from the Stokes and anti-Stokes intensity SERS signals, which originate from low- and high-energy vibrational levels, respectively.

The Raman spectra obtained for different excitation wavelengths show clearly that, for 785-nm excitation, the vibrational anti-Stokes peak intensities are much the same as the Stokes ones (**Figure 7***c*), in contrast to 532-nm excitation for which the anti-Stokes intensity is much lower than the Stokes intensity (**Figure 7***d*).

These results clearly indicate that 785-nm excitation fills the vibrational levels corresponding to anti-Stokes emission at 447 cm⁻¹ and 768 cm⁻¹, whereas 532-nm excitation does not. This is proof that direct electron transfer occurs only for discrete energies corresponding to specific orientations of the molecule on the NP and requires that the plasmon resonance energy matches perfectly some unpopulated hybrid NP–adsorbate energy levels.

5. CONCLUSION

Several methods are now available for creating tailored plasmonic surfaces. Although top-down methods remain quite useful, many innovative bottom-up methods using LB deposition, block copolymers, and NSL have been introduced. They are generally faster and cheaper and can be used on a larger scale. Combining top-down and bottom-up approaches also represents a strong trend. The past decade has witnessed the development of active molecular plasmonic devices. Many inputs have been used to change the properties of the molecular layer deposited on the plasmonic structures. When the dielectric function of the molecular layer around NPs in far-field interaction is changed, modulations of the LSPR properties generally remain small unless thick layers or CPs are used, but they are enhanced when the plasmon extinction matches the molecular absorption. When the active layer acts on the coupling strength of two NPs in near-field interaction (NP dimers), large modulation of the LSPR is observed. The plasmon excitation of dimers bridged by a molecule leads to two major effects: a shift in the frequency of the plasmon resonance and the production of hot charge carriers. The first effect is used for the realization of sensors and active plasmonic devices. Charge carrier generation (electrons and holes) accompanying the plasmon resonance is a phenomenon of great importance that is finding new applications in photocatalysis and photovoltaics; it was recently used in studies combining molecular plasmonics and molecular electronics. However, its efficiency is still debated, and a direct mode of electron transfer is required to bypass the cooling process in the metal. Recent results tend to indicate that direct transfer occurs toward particular excited vibrational states of the molecule.

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