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# Plasmon-mediated surface functionalization: new horizons for the control of surface chemistry at the nanoscale

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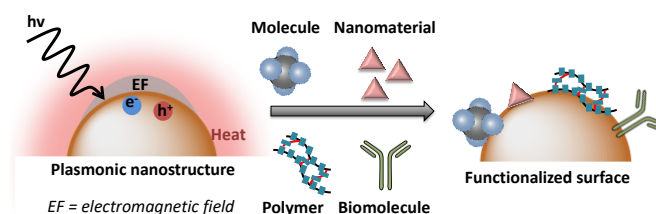
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**ABSTRACT:** The combination of plasmonics and surface chemistry is a fastgrowing field of research, with promising prospects for a wide range of applications, including analytical chemistry, sensing, photocatalysis, photovoltaics and nanomedicine. It takes advantage of the confined electromagnetic fields, local heat generation and hot carrier excitation, that accompany plasmon resonances to incorporate molecular functionalities into engineered nanomaterials with a spatial control at the nanoscale. This review aims to provide a concise overview of the main plasmon-mediated surface functionalization strategies developed so far, and explains how it renews the toolbox of surface chemistry approaches. Plasmon-mediated surface functionalization appears to offer an unprecedented fast and cheap large scale “bottom-up” approach to trigger site-selective surface functionalization and place molecules/nanomaterials into highly reactive regions (reactive spots) or high electromagnetic field regions (hot spots).

## 1. INTRODUCTION

Nanoplasmonics is a fastgrowing field of research, since the discovery of surface-enhanced Raman scattering (SERS) effect in the mid-1970s.<sup>[1]</sup> The SERS effect provides a strong enhancement of the Raman spectra of molecules adsorbed on noble metal nanostructures<sup>[2-5]</sup>. It arises from the excitation of localized surface plasmon (LSP) modes by electromagnetic waves in the UV to near infrared range, due to the collective oscillations of conduction band electrons at the particle surface<sup>[6-8]</sup>. These strong enhancements of the electromagnetic field were also widely exploited for metal-enhanced fluorescence (MEF) and surface-enhanced infrared absorption (SEIRA)<sup>[6]</sup>, providing powerful tools for the identification of analytes at low concentrations, moving the detection limits down to the single molecule level. Besides strong field enhancements, plasmonic nanostructures also exhibit intense extinction bands (absorption and scattering) in the visible and near-infrared spectral region, which peak wavelength  $\lambda_{\max}$  depends on the nanoparticle (NP) size, shape, chemical nature and local dielectric environment. This sensitivity to their close environment allows them to act as transducers for real-time chemical and biological sensing<sup>[9]</sup> since the binding of analytes to the particle surface induces changes in the local refractive index that can be detected through spectral shifts of the LSP wavelength. Absorption of light by plasmonic nanoparticles can also be nonradiatively relaxed, resulting in a highly localized heat energy release in the close proximity of NPs. Plasmonic NPs can thus be used as nanosources of heat for photothermal therapy applications<sup>[10]</sup>. In addition, charge carriers with high energy are generated upon nonradiative plasmon decay<sup>[11]</sup>. The resulting hot electrons and holes were shown to induce chemical reactions and activate bond formation and/or dissociation, opening up promising prospects in photocatalysis and industrial applications<sup>[12]</sup><sup>[13]</sup>. Plasmonic properties were also widely exploited for cutting-edge applications in photovoltaic<sup>[14]</sup>, imaging<sup>[15]</sup>, and optical trapping<sup>[16]</sup>. Besides, these recent years have witnessed the development of a new research field emerging

from the combination of plasmonics and surface chemistry. It takes advantage of the confined electromagnetic fields, local heat generation and hot carrier excitation, that accompany plasmon resonances to incorporate molecular functionalities into engineered nanomaterials with a spatial control at the nanoscale. While a variety of techniques have been reported to spatially control chemical functionalities on nanostructures, such as dip-pen lithography<sup>[17]</sup>, inkjet printing<sup>[18]</sup> and direct laser patterning<sup>[19]</sup>, these methods are time-consuming and can hardly achieve sub-50nm resolutions. Plasmon-mediated surface chemistry offers an unprecedented fast and cheap large scale approach that uses the nano-localized plasmonic properties surrounding nanostructures, to trigger site-selective surface functionalization and place molecules/nanomaterials into specific reactive spots.



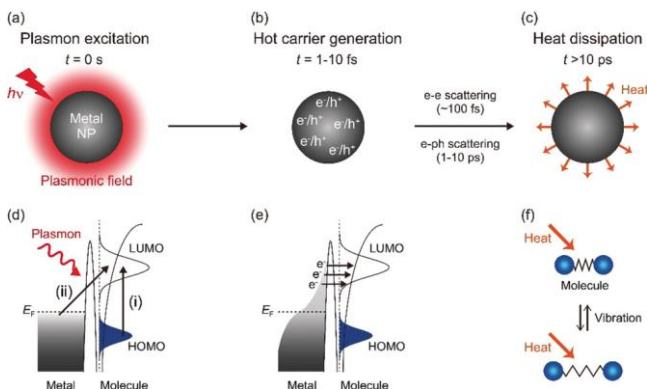
**Figure 1.** General scheme of plasmon-mediated surface functionalization and incorporation of surface functionalities derived from small molecules, polymers, nanomaterials or biomolecules.

This tutorial review aims to provide a concise overview of the main plasmon-mediated surface functionalization strategies developed so far for the control of surface chemistry at the nanoscale (Fig. 1), from hot-carrier driven processes and thermally activated surface modification to photopolymerization. The various plasmon-driven strategies will be divided into three main sections, focusing on the grafting of:

(i) molecular entities; (ii) polymer grafts; (iii) nanomaterials and macro-biomolecules (proteins, DNA). Perspectives of plasmon-mediated surface chemistry for future researches are also provided.

## 2. MECHANISMS OF PLASMON-DRIVEN SURFACE FUNCTIONALIZATION

The generation of strong electric field in the vicinity of plasmonic NPs upon LSP excitation, as well as hot carrier release and heat dissipation can be exploited to induce surface functionalization. The main mechanisms are illustrated in Fig. 2, and can be summarized as follows [20].



**Figure 2.** After LSP excitation of a metal nanostructure (a), hot carrier generation (b), and heat dissipation (c) take place. Surface functionalization can be induced through the following processes: (d) a direct intramolecular excitation (i), and charge transfer (ii); (e) an indirect hot-electron transfer, and (f) a local heating. Reproduced with permission [20]. Copyright 2019, Wiley-VCH.

Under light excitation (Fig. 2a), LSP leads to the emission of both photons by radiative decay and hot electrons and holes by non-radiative decay (Fig. 2b). These processes are very fast, with the generation of hot carriers after only 1-10 fs following LSP excitation. Then, heat dissipation from NPs to the surrounding environment takes place, as a result of thermal conduction (Fig. 2c). From these radiative and non-radiative decays, distinct processes of plasmon-induced surface functionalization have been proposed. A direct intramolecular excitation mechanism (Fig. 2d (i)), can take place. It is based on an electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of molecules, provided that the excitation of LSP is resonant with the transition energy of the two electronic levels of the molecules. In this process, LSP excitation acts as a local source of light to excite the molecules near the NP surface [21] and induce surface functionalization [22].

Another mechanism depends on a charge transfer between the metal surface and the molecules, from the metal energy states close to the Fermi level, to the LUMO of the adsorbed molecules (Fig. 2d (ii)). This transfer is possible provided that the energy of LSP corresponds to the energy gap between the LUMO and the metal states (near the Fermi level) [23].

Indirect hot-electron (Fig. 2e) or hot-hole transfer mechanism can also drive surface functionalization. The hot carriers generated upon LSP excitation are transferred from the metallic NPs to the molecules. In the case of hot electron transfer, the reaction is based on an inelastic electron tunneling to the adsorbed molecule, yielding a transitional negatively charged ionic state [24]. Similarly, the energetic holes of electron-hole pairs can be ejected from the plasmonic NPs into solution and take part to photo-oxidation reactions [25]. However, the lifetimes of hot holes are very short. Their accumulation at active sites, such as impurity, defects or adsorbed molecules is thus a key point for most hot holes-driven oxidation reactions [26].

The use of nano-localized heat dissipation following LSP excitation is another route to trigger surface functionalization. The temperature increase can be high enough to cross the potential energy barrier and activate surface reactions (Fig. 2f), such as thiol-ene click chemistry in the vicinity of gold nanostructures [27].

## 3. INCORPORATION OF SURFACE MOLECULAR FUNCTIONALITIES USING PLASMON-MEDIATED CHEMISTRY

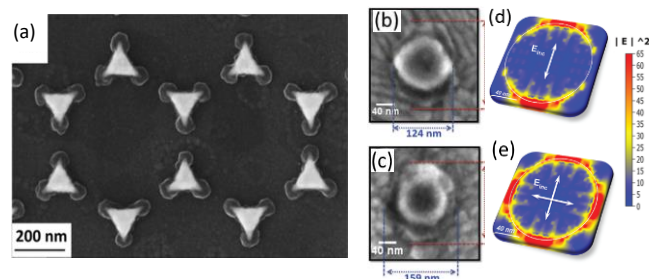
Control of surface chemistry of engineered nanomaterials is a critical issue for innovative applications in (bio-)sensing, catalysis and optics. Spatial control on the nanoscale of surface-grafted molecular species is particularly important in order to optimize the coupling between molecular functionalities and the underlying nanostructures. Several approaches, described below, were proposed to functionalize the whole surface or selective area of plasmonic nanostructures, using plasmon-mediated nano-localized hot carrier release.

### 3. 1. Plasmon-assisted surface grafting of molecular entities.

Literature has a wealth of different examples of spontaneous functionalization strategies in order to modify the surface of plasmonic nanostructures by organic molecules. Common methods [28] rely on the use of self-assembled thiol-based monolayers, carboxylate ligands, amines, aryl diazonium salts [29] and carbenes [30]. In contrast, the surface grafting of molecular entities promoted by LSPR excitation is an emerging research field and only few examples have been reported in the literature up till now. For example, a plasmon-mediated approach was proposed as a new way to facilitate the surface modification of gold-coated optical fibers by iodonium salts [31]. While classical approaches for surface modification by iodonium salts require complicated procedures (aggressive agents, strong bases), the plasmon-mediated strategy offers an alternative convenient approach that can be performed under mild reaction conditions. The mechanism relies on the plasmon-induced cleavage of the C-I bond of iodonium salts, generating highly reactive aryl radicals able to bind to the gold surface *via* covalent gold-carbon bonds, as proven by surface enhanced Raman spectroscopy ( $\nu_{Au-C}$  at ca. 436-453  $\text{cm}^{-1}$ ). This strategy

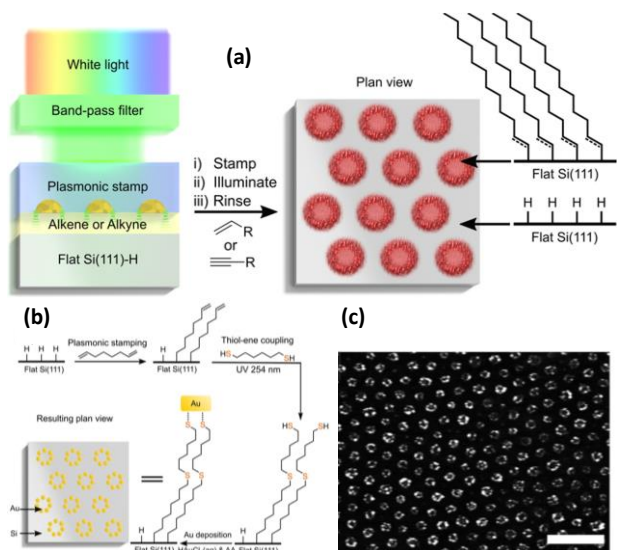
was employed to modify macroscopically the surface properties (hydrophobicity, antifouling properties) of optical fibers, using di-[3,5-bis(trifluoromethyl) phenyl]iodonium tetrafluoroborate. The grafting of fluorine-rich organic layers resulted in surface hydrophobicity, water repellence, and antifouling properties. All these characteristics are valuable for minimizing surface contamination of optical fibers used as biosensors in biological media, preventing biofouling and limiting their loss of activity in the long-term. Beyond macroscopic surface modification approach, LSP excitation could also trigger regioselective surface functionalization [32-34]. This was achieved for example *via* the site-selective hot-electron mediated reduction of aryl diazonium salts, generating aryl layers covalently attached on gold nanostructures through Au-C linkages and located specifically in the regions of maximum near field enhancement (see Fig. 3). For example, the plasmon-induced grafting of aryl layers derived from bithienylbenzene diazonium salts on Au nanotriangles was performed under visible-light illumination in a few minutes, without requiring the presence of any reducing agent [32]. As observed in Fig. 3a, the grafting process was highly enhanced on the triangle apex and between adjacent AuNPs, corresponding to the plasmonic hotspot area. The localization of the grafted layers was found to depend directly on the polarization of the incident light. Control of light polarization thus allows constraining the localization and anisotropic growth orientation of the deposited polyaryl layer on the nanotriangle surface, opening promising prospects in the field of “plasmonic electrochemistry”. Gold nanowires [33] and nanorods [34] were also functionalized using plasmon-mediated reduction of aryl diazonium salts, resulting in a regioselective grafting of organic patches around the nanostructures. This strategy showed several advantages compared to common classical approaches: (i) the grafting under plasmon excitation is very quick, with lengths of time that vary typically between few seconds to few minutes, while usual methods require several hours; (ii) the thickness of the organic coating can be varied from thin (ca. 1-3 nm) to thick poly(aryl) layers (up to 40–80 nm); (iii) the organic patches are spatially confined on the hot spot regions around the nanoparticles, *i.e.* the regions of maximum field enhancement. The incident light energy and LSP wavelength appeared to be critical factors to control the localization and thickness of the attached organic layers derived from diazonium salts. Extension of these strategies to the multi-functionalization of surfaces was proposed as a major breakthrough in surface chemistry, with the possibility to attach various chemical functions onto distinct nanoscale regions [35]. The multifunctional grafting under plasmonic near-field excitation was triggered by the change of polarization of incident light. As a proof of concept, the surface chemical properties of plasmonic gold nanodisks was patterned by two different types of functional polyaryl layers, bearing either carboxyl or hydroxyethyl pendant groups. The regioselective grafting of the polyaryl layers on the gold nanodisks occurred specifically in the regions of maximum field enhancement along the polarization direction, as shown in SEM images Fig. 3b-c, in good agreement with discrete-dipole approximation

(DDA) calculations (Fig. 3d-e). This double functionalization strategy opens up promising perspectives in molecular sensing, nanooptics and nanoelectrochemistry.



**Figure 3.** (a) SEM image of Au triangles after 4 min irradiation with visible light, in the presence of bithienylbenzene diazonium salt aqueous solution. Reproduced with permission.[32]. Copyright 2017, American Chemistry Society. (b,c) SEM images of Au NPs after plasmon-induced grafting of (b) carboxyphenyl layers derived from aryl diazonium salts, along the vertical direction and (c) additional hydroxyethyl phenyl layers along the horizontal axis. (d, e) Mapping of the near-field intensity enhancement upon illumination along the vertical axis (d) and both horizontal and vertical axes (e), using the DDA method. (b-e) Reproduced with permission.[35] Copyright 2018, Royal Society of Chemistry.

Another strategy based on “plasmonic stamps” was proposed to achieve nanopatterned surface chemistry on silicon [36]. The plasmonic stamps were made of gold nanopattern arrays embedded within a PDMS stamp. Under plasmon excitation, the stamps could trigger the nanolocalized hydrosilylation of alkenes or alkynes on a hydrogen-terminated silicon surface (see Fig. 4a). The interfacial hydrosilylation reaction was supposed to proceed *via* the generation of a proximal electric field in the silicon surface upon plasmon excitation, resulting in the production of charge carriers. Hexagonal arrays of nanoscale alkyl and alkenyl patches, with sub-100 nm pattern resolution, could be formed on the silicon surface using this approach, mirroring the topographic features of the parent gold nano-arrays. A subsequent thiol-ene coupling with 1,6-hexanedithiol on the free terminal alkene groups followed by electroless deposition of gold from aqueous HAuCl<sub>4</sub> solution and ascorbic acid (Fig. 4b) allowed clearly visualizing the created nanopatterns (see SEM image in Fig. 4c). The use of plasmonic stamps [37] thus appears as a valuable cost-effective alternative to photo-lithography of semi-conductor surfaces.

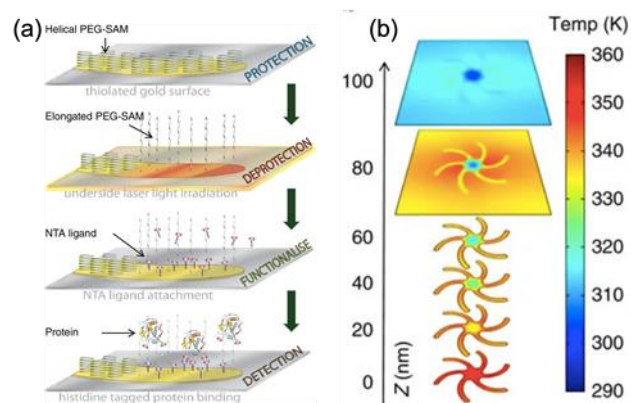


**Figure 4.** (a) Representative scheme of plasmon-induced hydrosilylation on silicon Si(111)-H surface using plasmonic stamps. Light illumination through the transparent PDMS stamp allows LSPR excitation of Au nanopatterns, resulting in localized hydrosilylation of alkenes or alkynes. (b) Scheme of plasmonic stamping followed by thiol-ene coupling and electroless gold deposition. (c) SEM micrographs of the resulting gold nanopatterns. Scale bars is 200 nm. Reproduced with permission.<sup>[36]</sup>. Copyright 2016, American Chemical Society.

**3.2. Plasmon-assisted surface post-functionalization.** Aside from directing the grafting of molecular entities on nanoscale regions of bare uncoated nanostructures, as described in the previous section, plasmon excitation can also be used to modify and post-functionalize the surface chemistry of molecular entities already grafted on the surface. For example, plasmonic properties were exploited to induce localized thiol-ene “click” chemistry reactions on gold nanostructures functionalized with allyl mercaptan self-assembled monolayers (SAMs)<sup>[27]</sup>. The “click” reaction was based on the addition of the thiol end groups of thiophenol to the alkene groups of SAMs. While this kind of reaction is usually performed under UV light or thermal activation, in the presence of a radical initiator, the nanoplasmonic effect allowed obtaining thiol-ene coupling in the visible range, even under unfavourable experimental conditions. This experiment thus demonstrated that the combination of plasmon-induced photonic and thermal effects can be exploited to induce nano-localized surface click chemistry.

In another example, chiral plasmonic nanostructures were used as nanosources of heat to induce thermal transformation of thermally responsive protective thiol SAMs, modifying their conformation from helical to elongated form, thus freeing up space for adsorption of ligands and biomolecules (see Fig. 5a)<sup>[38]</sup>. Although thermoplasmonic phenomena are well-known to generate fast heat dissipation and uniform temperature at the nanostructure surface, they also lead to temperature gradients in surrounding water (Fig. 5b) which were exploited in this original strategy. Pulsed laser irradiation of the SAMs-coated plasmonic

nanostructures resulted in localized water heating and spatially localized deprotection, promoting subsequent adsorption of nitrilotriacetic acid ligands. This plasmon-mediated chemical strategy based on thermal gradients in the solvent around nanostructures opens up promising prospects for the nanoscale control of chemistry over macroscopic areas.



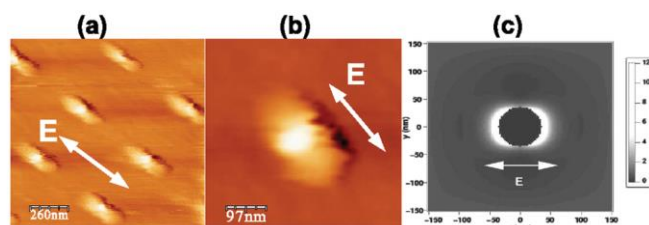
**Figure 5.** (a) Scheme of the protection/deprotection steps using a nanosecond pulse laser, and subsequent adsorption of nitrilotriacetic acid (NTA) ligands and proteins. (b) Stacked surface plot of thermal gradients in water at 8 ns (pulse end), with increasing height Z. Reproduced with permission.<sup>[38]</sup>. Copyright 2016, Nature Publishing Group.

#### 4. PLASMON-ASSISTED SURFACE POLYMERIZATION

The design of plasmonic nanoparticles with surface-grafted polymers has been the subject of many studies in a variety of fields, from (bio-)sensor devices<sup>[9]</sup> to drug delivery systems<sup>[10]</sup> and environmental decontamination. There are two pathways to elaborate a plasmonic surface coated with a polymer layer: in the first process, polymers can be “grafted to” the surface through a bearing group such as thiol or disulfide molecule. Yet, this process will not be discussed in this review to focus solely on processes that can be coupled with the excitation of plasmonic particles. In the second process, the polymerization is “from” the surface where active species initiate the covalent polymerization. Plasmon-induced “grafting from” polymerization techniques allow controlling the site-selectivity and polymer growth orientation, thereby expanding polymerization and nanofabrication toolbox. Different mechanisms can be enhanced by plasmonic effects, from free radical photopolymerization to controlled radical polymerization and hot carriers-initiated polymerization. In the following section, we review these various “grafting-from polymerization” methods that can be promoted by localized surface plasmon resonance (LSPR) excitation in order to obtain nano-localized polymer grafts on the surface.

**4.1. Plasmon-mediated free-radical photopolymerization.** Photoinduced free-radical polymerization is routinely used for the elaboration of commercial coatings, adhesives and for photolithography. It is based on the photoinduced production of radical reactive species able to initiate polymerization. In the last decade, questions have been raised about

the possible confinement of this process on plasmonic NPs: can the enhanced electromagnetic fields generated upon LSP excitation trigger a nanoscale photopolymerization process on the surface? The possibility to exploit the near-field enhancement to achieve nano-localized photopolymerization was studied in numerous papers using different nanostructures, such as silver spheres, cubes, and gold triangles. These studies evidenced several key parameters including the wavelength, polarization and energy of the incident light<sup>[39,40]</sup>. For example, Bachelot *et al.* showed that the spectral overlap between the LSPR and the absorption of the photoinitiator is part of the prerequisite experimental conditions to trigger plasmon-assisted photopolymerization<sup>[41]</sup>. Additionally, knowledge of the incident light energy dose threshold ( $D_{th}$ ), which corresponds to the lowest energy required to induce photopolymerization is of great importance. Indeed, energy doses higher than  $D_{th}$  result in a complete coating of the surface<sup>[22]</sup>. In order to induce the polymerization process locally by plasmon-mediated mechanism, the incident light energy dose should be set under  $D_{th}$ . Remarkably, using an energy dose four times weaker than  $D_{th}$ , and playing on the incident light polarization, the authors succeeded to generate two well-separated organic lobes around silver nanospheres,<sup>[40]</sup> as observed by AFM (Fig. 6a-b). The organic coating was made of polymeric patches adsorbed on the surface *via* non-covalent interactions. The spatial extent of the patches was found to coincide perfectly well with the two-lobe pattern characteristic of a dipolar near-field distribution, as calculated by finite-difference time-domain (FDTD) calculation (Fig. 6c). This resulted in a controlled breaking of the symmetry, from  $C_{\infty v}$  before plasmon-induced polymerization<sup>[42]</sup> to  $C_{2v}$  after the growth of the two polymer lobes, inducing the breakdown of SPR spectral degeneracy with the appearance of two artificial plasmon eigenmodes. The polarization response of LSPR was strongly correlated with the anisotropic polymerization around the particles. This approach thus provides a means for covering the NPs with a dielectric ellipsoid nanoscale coating and controlling by this way their optical behavior.



**Figure 6.** (a,b) AFM images of Ag NPs obtained after plasmon-mediated free-radical photopolymerization, under polarized light. (c) FDTD calculation of the electric field intensity distribution around Ag NPs ( $\lambda = 514$  nm). The white arrow indicates the incident light polarization. Reproduced with permission.<sup>[40]</sup> Copyright 2007, American Physics Society.

Besides, the strong localized field enhancement in the vicinity of lithographic NPs could be used for photolithographic imprinting to yield ultrasmall ( $<30$  nm) SU8 photoresist nanodots, *via* two-photon polymerization<sup>[43, 44]</sup>. Although the feature size reached with this nanolithography method is higher than the one that can be achieved using electron

beam lithography (down to 10 nm), the photo-pattern resolution is very low, corresponding to  $<\lambda / 25$ . One feature of particular interest is the possibility to address different resonances in one plasmonic system by the appropriate wavelength and polarization selection, allowing a single mask to provide various organic patterns. This offers promising prospects for programmable lithography.

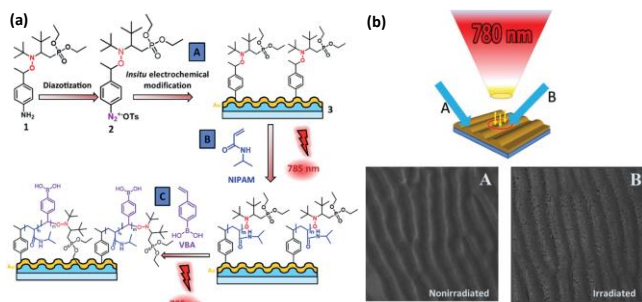
Photolithographic imprinting was used also as a convenient method to quantify field strength distribution in plasmonic nanostructures. For example, Misawa *et al.* achieved a quantitative measurement of the near-field enhancement around gold nanotriangles, using two-photon polymerization<sup>[45]</sup>. The NPs were first deposited on a surface and covered by a resist film (SU-8). After exposure to laser pulses, the resist was developed and the sample imaged by SEM. The nonlinear character of two-photon polymerization allowed high spatial resolution. The authors could correlate the threshold of SU-8 two-photon polymerization on the surface of the nanostructures with the Gaussian intensity profile of the pulsed laser, giving new insights into the near-field intensity around nanotriangles.

#### 4.2. Plasmon-mediated controlled radical polymerization.

Compared to conventional free radical polymerization, controlled radical polymerization (CRP) methods allow the preparation of well-defined polymers with controlled molecular weight and chain architecture, low polydispersity and site-specific functionality<sup>[46]</sup>, thus offering unprecedented opportunity in material chemistry. In these approaches, the long lifetime of growing chains offers new opportunities in polymer design, such as chain end-functionalization and chain extension. Among CRP approaches, nitroxide-mediated polymerization (NMP) is a reversible deactivation radical polymerization technique based on a nitroxide initiator, acting as a control agent (persistent radical) to generate well-defined functional and complex macromolecular architectures with very low polydispersity index. However, because the initiation requires thermal C-ON bond homolysis of the alkoxyamine initiators to form carbon-centered radicals and nitroxide, NMP is usually performed at elevated temperatures, above 100 °C, which constitutes the main limit of this technique. Plasmon-mediated homolysis of alkoxyamines was proposed as an alternative by O. Guselnikova *et al.*<sup>[47]</sup> to get over this difficulty. The alkoxyamine groups were first attached *via* covalent Au-C bonds to gold gratings through the electroreduction of the corresponding aryl diazonium salts (Fig. 7a, step A). The plasmon-induced homolysis and initiation of NMP were then triggered, at room temperature, by simple irradiation of the gratings with sunlight or with a laser beam under mild experimental conditions, allowing the preparation of poly(N-isopropylacrylamide)-co-4-vinylboronic acid block copolymers (step B and C, Fig. 7a). As derivatives of boronic acids are attractive recognition units for the sensing of carbohydrate derivatives,<sup>[48, 49]</sup> the obtained polymer-coated gold grating platforms were evaluated as smart SERS-sensors for the detection of biologically relevant glycoprotein.  $\alpha$ -1 glycoprotein was chosen as the target analyte as it is a useful biomarker of clinical outcome in various diseases<sup>[50]</sup>. Thanks to the thermoresponsive character of PNIPAM<sup>[51-53]</sup>, the carbohydrate moieties could be entrapped in the vicinity of the plasmonic surface at elevated temperature,

thus increasing significantly the SERS signal intensities of the glycoprotein.

Another type of plasmon-activated “from surface” controlled radical polymerization was reported by M. Erzina *et al.* [54], based on reversible addition-fragmentation chain-transfer (RAFT). RAFT polymerization usually employs thiocarbonylthio compounds to control polymerization *via* a reversible chain-transfer process. The RAFT agent was first grafted at the surface of gold gratings through covalent Au-C bonds, using aryl diazonium salts as coupling agents. Then, plasmon excitation of the gold gratings functionalized with the RAFT agent, allowed to efficiently activate a polymerization initiator (AIBN) in the proximity of the nanostructures and to induce surface-assisted growth of PNIPAM (Fig. 7b). Interestingly, the mechanism of polymer growth appeared to be self-limited, as evidenced through time-dependent SERS and XPS measurements, providing new means to produce ultrathin smart polymer layers with well-defined structures.

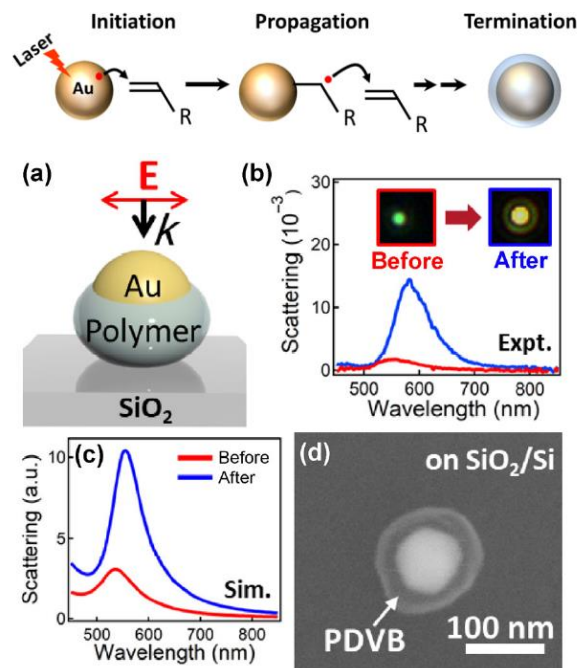


**Figure 7.** (a) Scheme of the strategy to achieve plasmon-induced “from surface” polymerization and growing of PNIPAM/PVBA brushes from alkoxyamine initiators-grafted gold grating. Reproduced with permission.<sup>[47]</sup> Copyright 2019, Royal Society of Chemistry. (b) SEM-EDX images of gold gratings functionalized with a RAFT agent, recorded on A) the non-illuminated area and B) the illuminated area (780 nm irradiation), revealing the formation of grafted PNIPAM brushes. Reproduced with permission.<sup>[54]</sup> Copyright 2018, Wiley-VCH.

### 4.3. “Hot-carriers”-initiated polymerization

**Hot-electron polymerization.** Plasmon-induced polymerization via hot carriers provides the opportunity to initiate locally most types of radical polymerization reactions. For example, the initiator-free polymerization of divinylbenzene (DVB), styrene and methyl methacrylate was achieved by hot electron initiation under light irradiation at a laser power lower than required for auto-initiation<sup>[55]</sup>. The light-triggered chain growth at the surface of plasmonic nanoparticles involved the initiation of free radicals *via* hot-electron transfer to monomers, in the absence of any initiators (see top scheme Fig. 8). AuNPs deposited on SiO<sub>2</sub>/Si wafer were used for hot electrons-initiated DVB polymerization, as illustrated in Fig. 8a. The bare and functionalized NPs exhibited distinguished optical properties, as observed under dark field microscope (inset of Fig. 8b). The scattering spectra of the coated AuNPs evidenced a red-shifted peak with respect to bare ones, in agreement with an increase of the refractive index due to the polymer coatings (Fig. 8b). These

experimental results were further supported by FDTD simulations (Fig. 8c). The covalently grafted polymeric layer could be visualized under SEM (Fig. 8d).

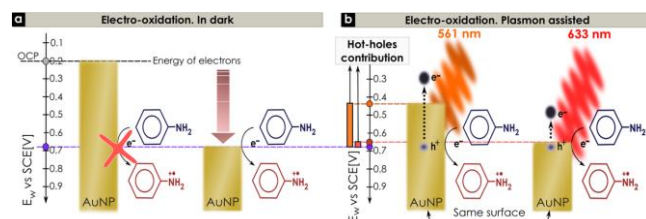


**Figure 8.** Top scheme and (a) Mechanism of hot-electron-initiated surface polymerization from AuNPs deposited on SiO<sub>2</sub>/Si wafer, using a pump laser ( $\lambda = 640$  nm, 2 mW, 60 s). (b) Scattering spectra of AuNPs before (red) and after (blue) laser irradiation. The insets display the dark field images. (c) Simulated scattering spectra of AuNPs before (red) and after (blue) laser irradiation. (d) SEM image of AuNPs after plasmon-induced polymerization of DVB. Reproduced with permission.<sup>[55]</sup> Copyright 2018, Springer.

The time- and power-dependent growth of this polymerization process allowed controlling both the thickness and orientation of the grafted polymer, which appeared to be highly influenced by the near-field distribution around the nanostructures and laser polarization. Interestingly, plasmon-mediated initiation of free radicals *via* hot-electron transfer to vinyl monomers was used by Baumberg and coworkers to enlarge locally the gap size between plasmonic nanoparticles<sup>[56]</sup>. Monomer polymerization within the nanogaps of gold NPs deposited on a gold mirror was shown to expand the nanogap volume, resulting in a strong blue-shift of the plasmon resonances. When the plasmon bands shifted too far away from the incident laser wavelength, the polymer growth ended. This self-limiting mechanism offers the possibility to tune the plasmon resonance bands to the desired spectral position.

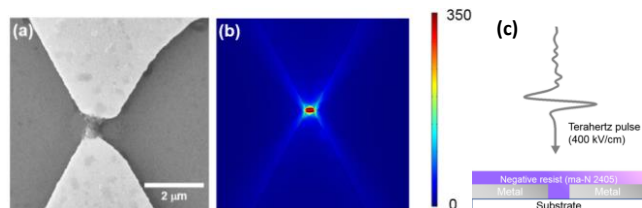
**Hot-hole polymerization.** Instead of exploiting hot electrons released under plasmon excitation, hot holes could also be used to trigger oxidative polymerization, such as the electro-oxidation of aniline to polyaniline<sup>[57]</sup> or pyrrole to polypyrrole<sup>[58]</sup>. Electro-polymerization of these monomer starts with their oxidation to form radical cations, which then react to form conductive polymers. As illustrated in Fig. 8 in the case of aniline polymerization, the reaction is

possible under an applied potential when there is an alignment of the electrode Fermi level and the highest occupied molecular orbital (HOMO) level of the monomer (see violet dash line in Fig. 9a, corresponding to the threshold potential to start the reaction,  $E_{\text{onset}} = 0.679$  V). In contrast, this cannot occur in open circuit potential conditions and in the dark because the Fermi level is higher than the HOMO of the monomers. Upon plasmon excitation under 561 nm laser illumination (left panel, Fig. 9b), the oxidation reaction is triggered at  $E_{\text{onset}} = 0.44$  V (orange dashed line), evidencing a 0.24 eV decrease of the energy required to start the polymerization reaction. The generation of hot holes thus facilitates electron transfer from the monomers, resulting in site-selective deposition of conductive polymer patches, located on the photoinduced oxidation active sites. It is noticeable that when the experiment was conducted under off-plasmon resonance illumination (633 nm), with increased laser power to obtain heating effect similar to that observed under plasmon excitation, the polymerization reaction was triggered at 0.65 V (right panel, Fig. 9b), close to the reaction potential in the dark. This result demonstrated that the heating effect was not the major cause for polymerization, but rather the generated hot holes.



**Figure 9.** Schemes of aniline electro-oxidation reaction (a) in the dark and (b) upon plasmon excitation at 561 nm or off-plasmon illumination at 633 nm. The violet dashed-line corresponds to the threshold potential to start the reaction in the dark,  $E_{\text{onset}} = 0.679$  V. The orange dashed line corresponds to  $E_{\text{onset}}$  (0.44 V) under plasmon excitation. The red dashed line corresponds to  $E_{\text{onset}}$  (0.65 V) under off-plasmon illumination conditions. Reproduced with permission.<sup>[57]</sup> Copyright 2019, American Chemical Society.

**Terahertz-driven polymerization.** For all the above-mentioned plasmon-mediated polymerization approaches, the optical excitation spectrum was limited from UV-visible to near-infrared region. When nanostructures exhibit LSPR in the longer wavelength range, the low energy of photons makes it difficult to promote photochemical reactions. Nevertheless, the possibility to extend plasmon-mediated polymerization to the terahertz (THz) frequencies was explored by W. Park *et al.*, using intense THz pulses to trigger polymerization of resists in nanoantennas<sup>[59]</sup>. The THz waves in nanoantenna were shown to induce the release of tunneling electrons in the area of high local field enhancement (the center of bowtie), resulting in nano-localized resist cross-linking (see SEM image in Fig. 10a and representative scheme of the process in Fig. 10c). The electric field profile was simulated using finite element method simulation (COMSOL), confirming that resist cross-linking occurred specifically in the regions of enhanced local field due to hot-electron emission (Fig. 10b). These results offer new possibilities to combine nano-photochemistry and terahertz optics.



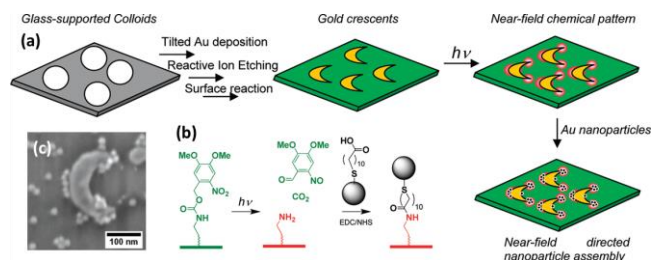
**Figure 10.** (a) SEM image of a bowtie antenna after terahertz-mediated resist cross-linking. (b) COMSOL simulations of the bowtie antenna evidencing high field enhancement in the center of the antenna. (c) Scheme of terahertz illumination to induce terahertz-mediated resist cross-linking. Reproduced with permission.<sup>[59]</sup> Copyright 2018, Nature Publishing Group.

## 5. PLASMON-DRIVEN SURFACE CHEMISTRY FOR SITE-SELECTIVE GRAFTING OF NANOMATERIALS AND BIOMOLECULES

Triggering the site-selective surface functionalization is crucial in order to place additional compounds, such as bio-functional molecules (DNA, proteins, amino acids) or nanomaterials into specific locations. For instance, the strategies discussed above can provide a strong confinement of coupling agents for the subsequent growth of polymer brushes, immobilization of gold nanoparticles<sup>[60]</sup>, quantum dots<sup>[61]</sup> or biomacromolecules<sup>[62,63]</sup>, with high lateral resolution. Interestingly, such post-functionalization is expected to occur exclusively on highly reactive or high electromagnetic field regions, while leaving the other area unmodified, offering new prospects for molecular sensing and nano-optics applications.

### 5.1. Site-selective immobilization of nanoparticles.

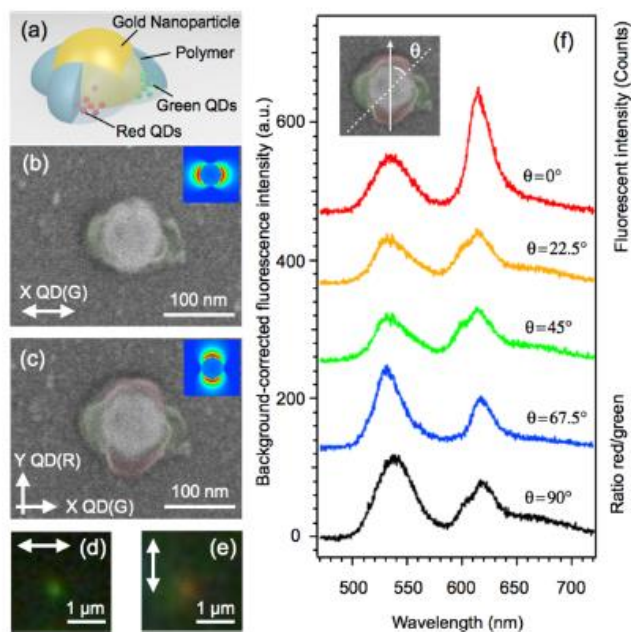
The very first attempt of site-selective immobilization of nanoparticles, after a plasmon-mediated surface functionalization, has been reported by K.H. Dostert *et al.* in 2012<sup>[60]</sup> on gold crescents-coated glass substrates. The glass surface was functionalized by a photosensitive organosilane exhibiting a terminal amine functionality caged with a photoremovable group. Upon gold crescents LSP excitation, the near-field enhancement was shown to trigger locally the photocleavage of the cage, leaving free amine groups on the glass surface, in the vicinity of the gold nanostructures.



**Figure 11.** (a) Multi-step strategy to achieve near-field driven chemical nanopatterns and guide regioselective and controlled assembly of gold colloids (b) Surface modification mechanism. (c) SEM image of a gold crescent modified by gold colloids after this multi-step strategy. Reproduced with permission.<sup>[60]</sup> Copyright 2012, American Chemical Society.



The scheme of this multi-step strategy is illustrated in Fig. 11a and the mechanism of surface functionalization is described in Fig. 11b. The resulting near-field driven chemical nanopatterns were used to guide the regioselective and controlled assembly of gold colloids (see SEM image in Fig. 11c), offering outstanding perspectives to trigger assemblies at the nanoscale. Other types of nanoparticles, such as quantum dots (QDs) could also be trapped at hot spots, as described in a recent paper by X. Zhou *et al.* [61], resulting in hybrid plasmonic-nanoemitters structures (see Fig. 12a). The site-selective immobilization of pentaerythritol triacrylate (PETIA)-grafted QDs was performed by LSP-triggered two-photon nanophotopolymerization of a formulation containing the quantum dots.



**Figure 12.** (a) Schematic representation of the plasmonic nanoemitters. (b,c) SEM images of gold nanodisks after LSP-triggered two-photon nanophotopolymerization of a formulation containing the QDs. The green QDs are immobilized along the X axis, while the red QDs are trapped along the Y axis. Insets show simulated dipolar near-field intensity (d,e) Far-field fluorescence images upon illumination polarized along X and Y. (f) Fluorescence spectra versus the incident polarization direction. Reproduced with permission. [61]. Copyright 2015, American Chemical Society.

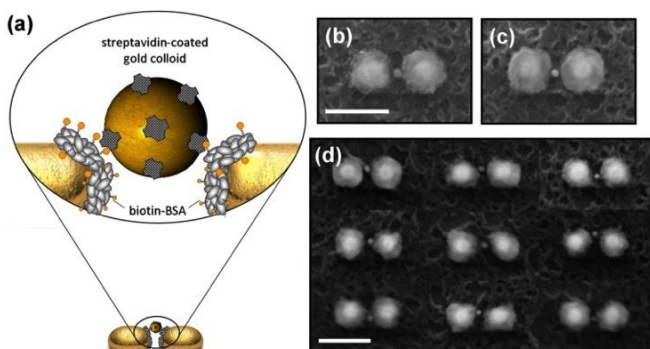
Interestingly, (as shown in SEM images (Fig. 12b-c) the polymerization process was confined regioselectively on two distinct areas around the plasmonic NPs, by playing on the incident polarization, along the X or Y axis. These experimental results were compared with the simulated dipolar near-field intensity (insets Fig. 12b-c) demonstrating a good agreement between the location of the deposited hybrid layers and the regions of intense electric field. The use of two different polymerizable solutions containing QD emitters of various colors (green and red emission) resulted in their selective immobilization along different orientations around the NPs, as demonstrated in the far-field fluorescence images in Fig. 12d-e. These two-color plasmonic nanoemitters thus display a dominant emission wavelength

that can be tuned by simply rotating the polarization of the incident light, as shown in the fluorescence spectra recorded at different incident polarization direction (Fig. 12f). The approach could be transposed from highly symmetric nanodisks to arbitrary shaped nanoparticles, such as nanostars, offering promising outlook for producing switchable plasmonic nanoemitters and developing addressable RGB nanopixels.

## 5.2. Site-selective immobilization of biomolecules.

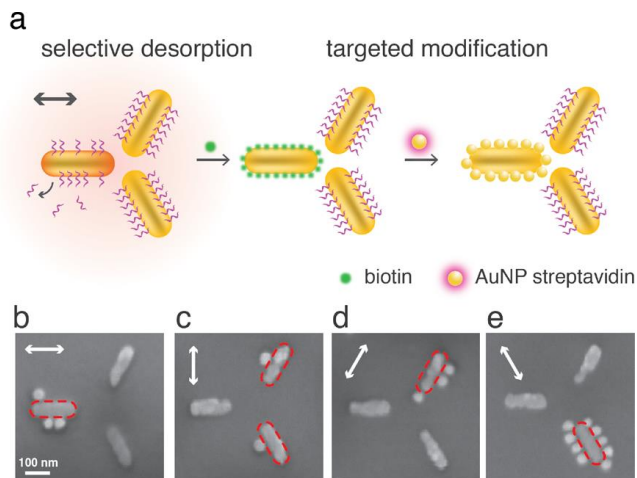
The enhanced local fields in hot spots were also exploited as the driving mechanism to trigger the nanoscale immobilization of proteins. This strategy was proposed as a way to maximize the interaction between light and analytes and thus the efficiency of nanophotonic biosensors. Indeed, electromagnetic fields generated under plasmon excitation are non-homogeneously distributed at the surface of plasmonic nanostructures and exhibit variable intrinsic properties. The possibility to trap the target biomolecules within selected area sustaining EM fields with optimized properties would be a major advance. Towards this end, Kadodwala and co-workers functionalized selective regions of chiral plasmonic arrays through local heating of surrounding water triggered by pulsed laser irradiation, as described in paragraph 3.2. This strategy was used to immobilize proteins in area sustaining EM fields of enhanced chiral asymmetry [38], thus improving biosensing efficacy. Remarkably, attomole detection of proteins such as Concanavalin A or His-tagged protein 5-enolpyruvylshikimate-3-phosphate synthase was achieved using plasmonic polarimetry experiments [64], while fully covered nanostructures resulted only in femtomole detection levels. The site-selective immobilization of proteins in hot spots could also be achieved by multiphoton plasmonic lithography, as reported by B. B. Raeva *et al* [63]. This method allowed confining cross-linked bovine serum albumin (BSA) hydrogel patches at the tips of gold nanotriangles. Inter-protein crosslinking inside the hydrogel layers was achieved using Rose Bengal (RB) as a photoinitiator. Interestingly, the photo-induced crosslinking reaction appeared to be only efficient on the sites of maximum electromagnetic field intensity enhancement, resulting in a regioselective grafting around the nanotriangles. The incident laser polarization and intensity were shown to be critical parameters to control both site selectivity and extent of hydrogel layer grafting. This approach thus offers a rapid and single-step strategy for the formation of gold nanotriangle-BSA hydrogel complexes and more generally for the nanoscale immobilization of proteins, opening up potential applications in biophotonics and life sciences. BSA proteins could also be immobilized into the nanometer-sized gap of plasmonic dimers, using light-assisted molecular immobilization (LAMI) via three-photon absorption, as shown by C. M. Galloway *et al.* [62]. The LAMI approach is based on the absorption of light by proteins, resulting in a disruption of disulfide bridges and formation of thiol groups, able to bind to the NP surface (see representative scheme in Fig. 13a). In this example, the binding of proteins was triggered by the enhanced plasmonic fields produced by the excitation of the

gold dimers at their LSPR. The nanolocalized grafted proteins were then used as a scaffold to anchor in the region of most intense field, additional nano-objects, such as streptavidin-gold colloids (see SEM images in Fig. 13b-d).



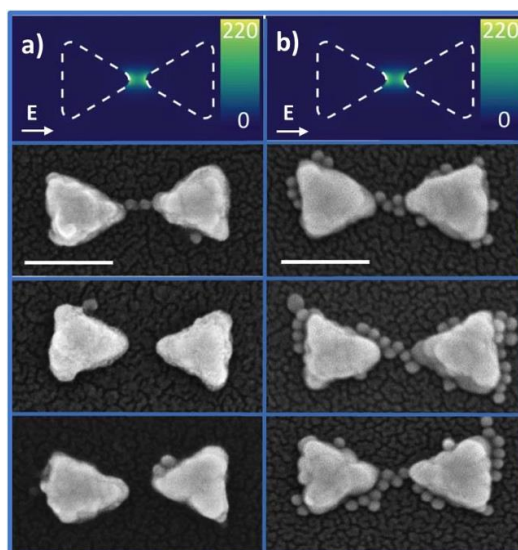
**Figure 13.** (a) Scheme of the plasmon-induced grafting of BSA proteins, further used as scaffolds to anchor gold colloids. (b,c,d) SEM images of gold dimers with one single Au NP trapped inside their gap. Scale bar = 150 nm. Reproduced with permission. [62] Copyright 2013, American Chemical Society.

Instead of exploiting the enhanced local fields in hot spots to trigger nanolocalized photo-induced surface functionalization, hot-electron-driven processes were also used to achieve site-selective positioning of nano-objects. For example, S. Simoncelli *et al.* [65] demonstrated the spatially-resolved cleavage of Au-S bonds in thiol self-assembled monolayers, based on the highly localized light-to-chemical-energy conversion of plasmonic gold nanorods. The localized reductive desorption of thiolated molecules was governed by the generation of hot-electrons and occurred only at the location of the maximum field enhancement, leaving accessible those locations for subsequent ligand replacement and post-functionalization. Tuning the wavelength and polarization of the incident light afforded on-demand patterning, which could be further exploited for the selective positioning of fluorescently labeled DNA or gold colloids. (Figure 14 illustrates this concept with the plasmon-induced nanolocalized desorption of thiol ligands at the surface of gold nanorod trimers followed by their replacement by thiolated biotin-terminal linkers and adsorption of streptavidin-coated 50 nm AuNPs. SEM images evidenced (Fig. 14b-e) the selective immobilization of AuNPs on one or two rods, depending on the polarization of the incident light used to desorb thiol ligands. These results demonstrate the potential of plasmon-driven desorption processes to design hierarchical nanoparticle assemblies.



**Figure 14.** (a) Scheme of plasmon-induced selective desorption of thiols on gold nanorods and targeted modification by gold colloids. (b-e) SEM images of the Au nanorods obtained after binding of 50 nm Au NP colloids. The white arrows indicate the incident light polarization. Reproduced with permission. [65] Copyright 2018, American Chemical Society.

Hot-electron driven nanoscale patterning of surface chemistry could be performed as well on silver bowties and rounded bar-dimer antennas (see Fig. 15), taking advantage of the capacity of hot electrons to induce the local reduction of 4-nitrothiophenol (4-NTP) self-assembled monolayers covering Ag NPs [66]. The plasmon-induced six-electron-mediated reduction generates locally 4-aminothiophenol nanopatterns able to react with specifically designed 15nm AuNPs capped with a carboxylic-acid terminated molecular layer to form interfacial amide bonds.



**Figure 15.** Top panels display FDTD simulations of near-field distribution on Ag bowties excited at 633 nm. Below are the SEM images of 15 nm AuNPs immobilized on 4-NTP-coated silver bowties after (a) 1 min and (b) 2 min of illumination at 633nm in 0.1M HCl, with parallel polarization. Scale bars, 100 nm. Reproduced with permission. [66] Copyright 2017, Nature Publishing Group.

As shown in SEM images (Fig. 15) recorded after parallel illumination during 1 min (Fig. 15a) or 2 min (Fig. 15b) in 0.1M HCl, the AuNPs are immobilized preferentially at the tips of the nanostructures, in agreement with FDTD calculations, but also on the edges and corners. The conversion reaction was found to be highly dependent on illumination time, with an absence of AuNPs immobilization in the case of only 30s illumination and a higher amount observed after 2 min compared to 1 min illumination. This simple, low-cost and large-scale approach could be extended to a wide range of plasmonic nanoantenna in order to confine nanomaterials into reactive spots or hot spots and further enhance the efficacy of photocatalysis, energy conversion and (bio)-sensing.

Table 1 summarizes the various plasmon-mediated surface functionalization strategies described in this review, for the immobilization of molecular entities, polymers, nanomaterials and biomolecules.

**Table 1.** Plasmon-mediated surface functionalization approaches.

NPs	Reaction/Mechanism	Surface agent	Ref.
<b>Immobilization of molecular entities</b>			
Au-coated fibers	Reduction/hot e <sup>-</sup>	Iodonium salts	[31]
Au nanorods, triangles, disks	Reduction/hot e <sup>-</sup>	Diazonium salts	[32-35]
Au nanodisks	Click chem./EM & $\Delta T$	Thiophenol	[27]
Chiral Au structures	Conformation change/ $\Delta T$	NTA ligand	[38]
<b>Immobilization of polymers</b>			
Ag NPs, Au dimer, Au nanocubes	Photopol./EM	Polyacrylate	[39-41]
Au nanotriangles	Two-photon pol./EM	SU-8	[45]
Au gratings	NMP, RAFT/EM	PNIPAM/PVBA	[47, 54]
AuNPs	Radical pol./hot e <sup>-</sup>	PS, PMMA, PVB	[55, 56]
AuNPs	Oxidative pol./hot h <sup>+</sup>	PANI, PPy	[57, 58]
Au Bowties	Terahertz pol./hot e <sup>-</sup>	Polymer resist	[59]
<b>Immobilization of nanomaterials and biomolecules</b>			
Au crescents	Photocleavage/EM	Gold colloids	[60]
AuNPs	Two-photon pol./EM	QDs	[61]
Au dimers	Three-photon pol./EM	BSA, gold colloid	[62]
Au nanotriangles	Cross-linking/EM	BSA hydrogel	[63]
Au nanorods	Reductive des./Hot e <sup>-</sup>	DNA, gold colloid	[65]
Silver bowties	Reduction/Hot e <sup>-</sup>	Gold colloids	[66]

EM/ $\Delta T$  = plasmon-induced electromagnetic field enhancement/thermal effect. Chem. = chemistry. Pol. = polymerization. Des. = desorption.

## 6. CONCLUSION AND OUTLOOK

This article provides an up-to-date review on the emerging research field of plasmon-mediated surface functionalization. The outstanding optical properties of localized surface plasmons supported by metal nanostructures appeared recently to offer the possibility of renewing the toolbox of surface chemistry approaches by: (i) controlling the nanoscale localization of surface molecular functionalities; (ii) regulating the thickness of polymer grafts as well as their composition and growth orientation; (iii) positioning functional molecules/nanomaterials on highly reactive regions (reactive spots) or high EM field regions (hot spots), while keeping most of the nanostructure surface chemically passive. Remarkably, plasmon-mediated surface functionalization techniques provide huge versatility due to the wide range of surface molecular entities, from small molecules to polymers, nanomaterials and biomolecules and the large choice of nanostructures, with various compositions, sizes and shapes. In addition, the manipulation of incident light characteristics, such as laser wavelength, power and polarization offers another level of versatility to tailor the spatial distribution of molecular functional layers. Interestingly, the near-field enhancement and photothermal effects were also exploited to perform plasmon-assisted nanolithography, achieving pattern sizes smaller than the diffraction limit expected in classical photolithography, without the need of any additional equipment or mask design. Reversely, these approaches appeared to be a fascinating way to map plasmon modes in nanostructures with a level of details comparable to that provided by advanced optical or electron-based techniques. They can be thus considered as indirect imaging methods, able not only to reveal the optical near-field response but also trace the hot carrier quantity and energy.

However, this fast growing field is still in its infancy regarding practical and real world applications. There remain many more challenges that need to be addressed before plasmon-driven surface functionalization methods achieve their full potential. From a theoretical point of view, much is left to learn about the hot carrier energy distribution, the various processes of energy transfer and the critical role of the interface. It will be also crucial to get new insights into the mechanistic details of plasmon-driven surface chemistry and to discriminate the contribution of hot carriers release from temperature effects and near-field enhancement, which may all contribute to chemical surface transformations. From a practical perspective, the design of nanostructure/organic layer interfaces with long-term stability in various environments and under plasmon excitation should be given attention. In addition, although plasmon-induced chemistry allows confining the functional layers within nanoscale area on the nanostructure surface, chemical passivation of the other parts of the surface still remains difficult to achieve and constitutes another promising research direction. Combining organic functional layers with nanomaterials or biomolecules is also an intriguing direction. With the huge quantities of emerging nanosized materials, multi-composite interfacial layers with other nanomaterials such as quantum dots, oxides or biosupramolecular entities may offer distinct added-value properties.

Finally, efforts are still required to further improve the analytical performance of these advanced nano-interfaces for (bio-)sensing applications and detection of trace amount of analytes.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Table of Contents

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