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Da Li, Théo Geronimi, Nordin Felidj, Philippe Nizard, Delphine Onidas, et al.. Surface modification of plasmonic nanomaterials with aryl diazonium salts. *Aryl Diazonium Salts and Related Compounds. Surface Chemistry and Applications*, pp.211-226, 2022, 978-3-031-04398-7. hal-03705870

HAL Id: hal-03705870

<https://hal.science/hal-03705870v1>

Submitted on 27 Jun 2022

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Surface modification of plasmonic nanomaterials with aryl diazonium salts

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Abstract

This chapter provides an overview of the various surface modification strategies based on the use of aryl diazonium salts for the functionalization of plasmonic nanoparticles. Aryl diazonium salts appear as a valuable alternative to commonly used thiol self-assembled monolayers due to several advantages, including the formation of robust interfacial metal-surface bonds, simple synthesis and surface grafting protocols, a large range of functional groups and the possibility to form multilayers around the nanoparticle surface. Owing to these outstanding features, the combination of aryl diazonium salts and plasmonic nanoparticles is receiving increasing attention for potential applications in various fields such as nanosensors, bioimaging, environment, forensic science and antimicrobial materials. This chapter describes the chemical processes involved in the surface modification of plasmonic nanoparticles by diazonium salts, the resulting nanohybrids and the targeted applications.

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1. Properties of plasmonic nanoparticles

Plasmonic nanoparticles (NPs) with unique chemical, physical and optical properties have attracted a lot of attention over the past decades. These NPs sustain a collective coherent oscillation of the free electrons at their surface upon electromagnetic excitation, called localized surface plasmon (LSP), as illustrated in Fig. 1.[1] When the frequency of the incident radiation matches the frequency of LSP modes, this results in LSP resonance (LSPR), which can be observed as intense extinction bands in the visible and near-infrared spectral range. The plasmon band wavelength depends on the NPs' composition, size, shape and surrounding dielectric environment. Therefore, the presence of analytes in the vicinity of plasmonic NPs can be detected by spectral shifts of the LSP wavelength, induced by changes of the local medium refractive index, allowing real-time chemical and biological sensing. The excitation of LSP is also accompanied by the generation of highly enhanced electromagnetic fields, which have been widely used in surface-enhanced spectroscopies, such as Surface-Enhanced Raman spectroscopy (SERS) to detect trace amount of analytes, down to the single-molecule level.[2] Besides, nonradiative relaxation of LSP results in heat energy release and production of hot carriers. The plasmonic NPs can thus act as nanosources of heat for photothermal applications or charge carriers (hot electrons and holes) to induce chemical reactions locally.[3]

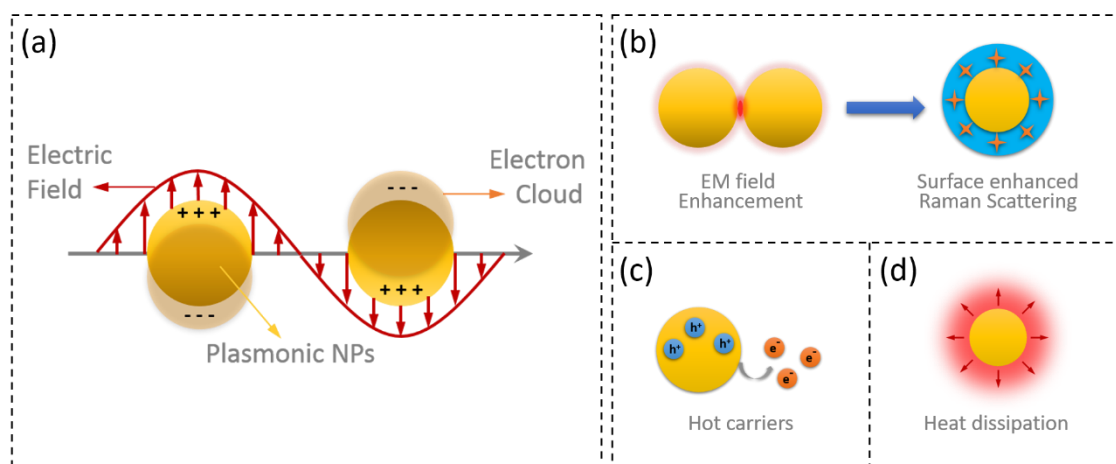


Figure 1. (a) Representative scheme of the collective oscillation of free electrons at the surface of plasmonic NPs. The excitation of LSP results in a cascade of effects, including: (b) a strong electromagnetic (EM) field enhancement which can be exploited for SERS, (c) the generation of hot carriers and (d) heat dissipation leading to local heating.

Among the different types of plasmonic NPs, gold and silver NPs (Au NPs and Ag NPs) have been the most widely studied. While the size and shape of the NPs are crucial parameters to optimize their optical properties, the control of their surface chemistry is also a critical issue as it determines the interaction between the NPs and their environment. Therefore, considerable efforts have been made in order to develop

appropriate surface modification strategies, with the aim to strengthen colloidal stability and to add new functionalities, thereby broadening the application scope of plasmonic NPs.

2. Common strategies for surface functionalization of plasmonic NPs

The main strategies for surface functionalization of plasmonic NPs are based on either physical adsorption or covalent bonding. Compared to physical adsorption, covalent bonding offers more robust interactions between the NPs and the immobilized molecules, thus improving interfacial stability. The most common strategy consists in using thiol ligands resulting in the formation of thiolate self-assembled monolayers (SAMs), anchored on the NPs surface via gold–sulfur bonds. [4] Thanks to the rich chemistry of gold–sulfur bonds, a wide variety of functional groups have been attached around the plasmonic cores leading to innovative hybrid nanomaterials.[5] However, issues regarding the chemical stability of SAMs have been identified. For example, they have been shown to desorb spontaneously from surfaces after few days in aqueous solutions.[5, 6] Moreover, they degrade upon laser excitation[7] and can be exchanged in biological media, jeopardising their efficacy and reliability. Although significant improvements have been obtained *via* the use of longer-chain thiols, multidentate sulfur-based adsorbates, silica coatings or small amounts of amphiphilic surfactants, the development of alternative approaches to obtain strong covalent anchoring of surface functions onto the plasmonic cores still remains an important challenge.

3. Surface functionalization of plasmonic NPs with aryl diazonium salts

A recent approach has emerged for the functionalization of plasmonic nanomaterials based on the use of aryl diazonium salts. General formula of aryl diazonium salts can be expressed as A^- , $^+N_2-C_6H_4-R$, where A^- is the counter-ion and R stands for the chemical function on the aromatic ring. Since Jean Pinson and coworker's pioneering work in 1992 described the mechanism of electrochemical reduction of aryl diazonium salts to modify glassy carbon electrodes,[8] these compounds have attracted widespread attention in the field of surface chemistry. Indeed, the cleavage of N_2 from diazonium salts occurs at low potential and on reducing surfaces opening promising prospects as surface functionalization agents in various applications including nanomedicine, forensic science, sensors, catalysis and energy. These compounds offer several advantages over other common strategies, such as their ease of synthesis, their fast grafting on surfaces, the large choice of available functional groups and the formation of robust covalent interfacial bonds with the surface. Generally, their grafting on NPs involves a two-stage mechanism. Firstly, the decomposition of the diazonium salts generates an aryl radical able to bind on the surface. In a second step, the formed highly reactive radicals react with the already grafted groups resulting in nanometer to micrometer thick polyaryl layers. To obtain functionalized NPs, diazonium salts can be used either as isolated compounds or can be generated *in situ*. The use of isolated salts allows to control the initial concentration of

the reactants. However, the long-term stability of the diazonium salt solids and solutions is a major concern. The use of in situ generated aryldiazonium salts from the corresponding aromatic amines can overcome this issue and achieve high grafting densities on the NPs while preserving colloidal stability. Several approaches have been proposed to modify plasmonic nanomaterials by diazonium salts.[9] The main ones based on electrochemistry, addition of reducing agents, spontaneous reaction or plasmon-mediated chemistry, are described below (Fig. 2).

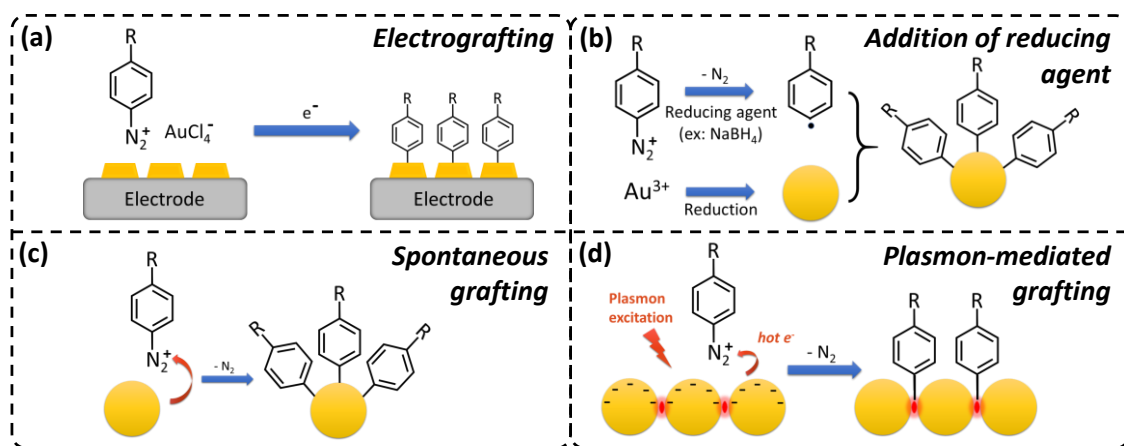


Figure 2. Representative scheme of the main approaches for the surface modification of plasmonic NPs by aryldiazonium salts, *via* (a) electrografting; (b) addition of a reducing agent¹; (c) spontaneous reaction between the diazonium salt and the NPs and (d) plasmon-mediated reduction of diazonium salts.

3.1 Electrografting

As aryl radicals can be generated by electrochemical route, electrografting of aryl diazonium salts has become a powerful method to functionalize supported plasmonic NPs. For example, arenediazonium tosylates could be deposited on plasmon-active Au and Ag thin films *via* either spontaneous reactions or electrochemistry (see Fig. 3).[10] Interestingly, the spontaneous grafting results in thin monomolecular layers with potential interest for Surface Plasmon Resonance (SPR) technique or SERS sensors while electrochemical activation generates thick polyaryl layers opening promising prospects for applications in tunable plasmonic devices and plasmon-based lasers. In another example, aryl diazonium salts were electrografted *via* pulse deposition and used as antifouling coatings onto Au-based SPR sensors.[11] The antifouling performances of the coatings obtained from diazonium salts bearing different functional groups or alkanethiolate self-assembled monolayers were compared, revealing an enhanced antifouling behavior in the case of 4-phenylalanine diazonium chloride with a significant

¹ For the sake of clarity, the scheme (b) depicts only the case of the simultaneous reduction of auric and isolated diazonium salts. The mechanisms based on the phase transfer of diazonium cations to $[\text{AuCl}_4]^-$ phase or on the reduction of benzenediazoniumtetrachloroaurate(III) complexes by sodium borohydride are not represented.

reduction of the nonspecific adsorption surface coverage of crude bovine serum proteins (down to $42 \pm 4 \text{ ng/cm}^2$). Proteins, modified with an aryl-diazonium adduct, could be also electroaddressed onto gold SPR imaging (SPRi) chips for the detection of antibodies and ovalbumin.[12] This approach yielded multiple spots of robustly anchored proteins distributed over the SPRi biochip for the detection of antigen/antibody interactions.

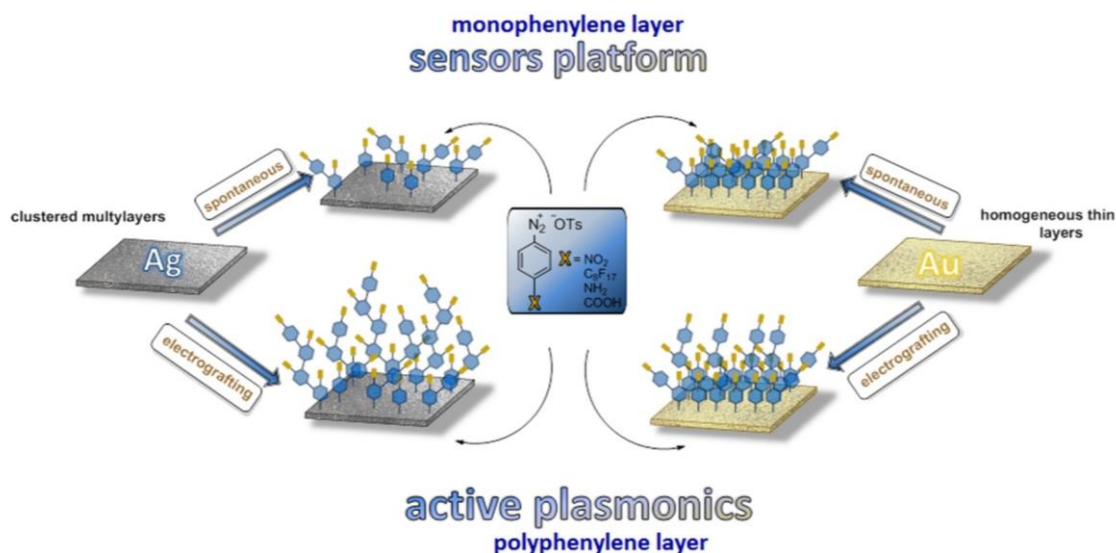


Figure 3. Representative scheme of the functionalization of plasmon-active Au and Ag thin films by arenediazonium tosylates: spontaneous reactions or electrochemistry. Reproduced with permission from ref.[10]. Copyright, 2017, Elsevier.

3.2 Spontaneous grafting or chemical reduction

Contrary to macroscopic surfaces for which electrografting of diazonium salts is mostly used, it becomes tricky in the case of colloidal NPs. Therefore, for colloidal NPs, spontaneous reactions or addition of a reducing agent in the medium appears as simple alternatives to generate radicals from aryldiazonium salts. The spontaneous grafting is a straightforward approach consisting to mix the NPs with the diazonium salts and to let it react at room temperature, in the presence of air, as described by McDermott et al. [13]. This simple process was proved to preserve the colloidal stability of the nanohybrids and to yield strongly anchored organic shells with the desired functionality on the NP surface. The possibility to obtain, with this approach, multifunctional layers with various chemical groups around the plasmonic cores, as illustrated in Fig. 4, was assessed using SERS, with the presence of different tags around the NPs.[14] Au NPs functionalized by aryl groups were also obtained *via* the phase transfer of diazonium cations to $[\text{AuCl}_4]^-$ phase,[15] the simultaneous reduction of auric and isolated diazonium salts [16] or through the reduction of the benzenediazoniumtetrachloroaurate(III) complexes by sodium borohydride (NaBH_4).[17] The resulting NPs were shown to withstand long periods of sonication in various solvents and remained perfectly stable in the solid state, in ambient conditions.

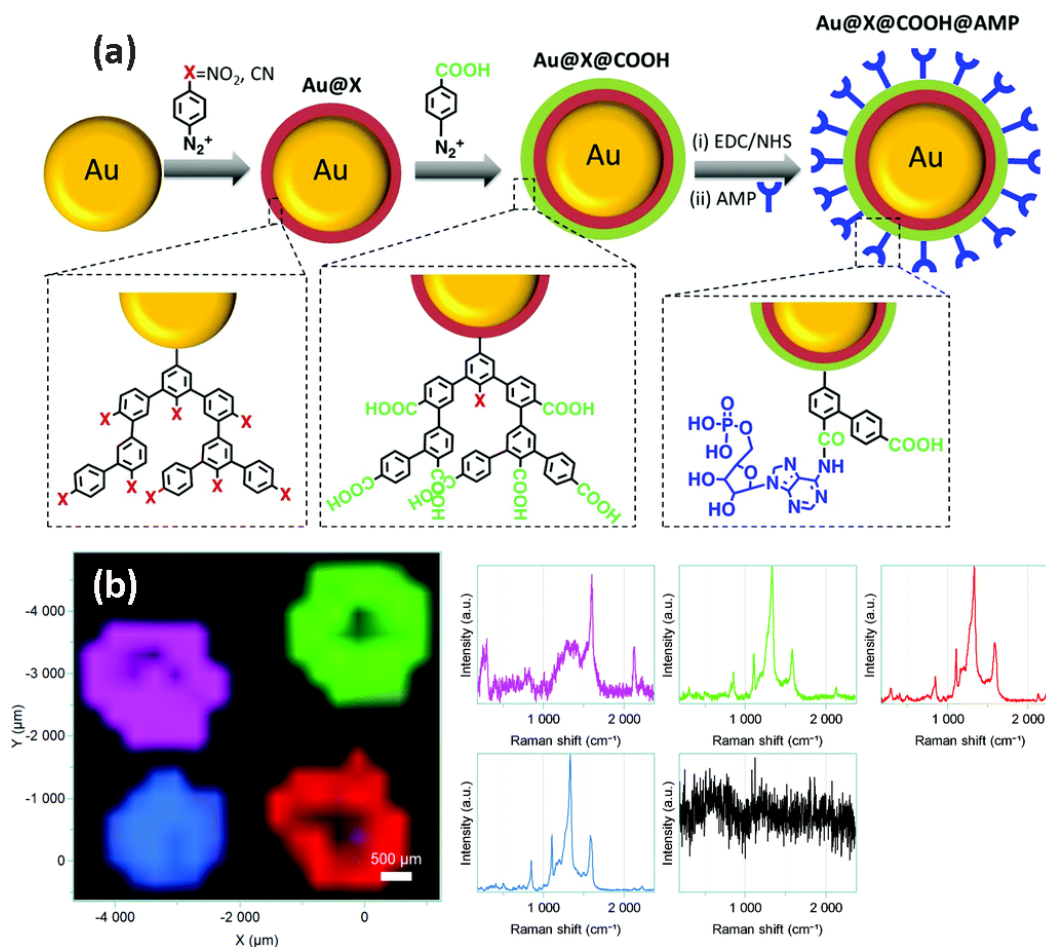


Figure 4. (a) Representative scheme of the spontaneous grafting of aryl diazonium salts on Au NPs and formation of multifunctional layers; (b) Raman images of dried drops of Au@CN (magenta), Au@NO₂ (blue), Au@CN@NO₂ (green) and Au@NO₂@CN (red), and their corresponding Raman spectra. Adapted from ref. [14]. Copyright, 2020, Royal Society of Chemistry.

3.3. Plasmon-mediated grafting

Another approach to reduce aryl diazonium salts at the surface of plasmonic NPs consists of taking advantage of the “hot electrons” produced by the excitation of surface plasmons. Hot electrons are generated in nano-localized area around the NP surface, sustaining a strong near field enhancement, resulting in site-selective hot-electron mediated reduction of diazonium salts. This plasmon-mediated surface functionalization approach thus offers an unprecedented “bottom-up” approach to place molecules or nanomaterials into reactive area or high electromagnetic field regions (hot spots). It was used for the regioselective functionalization of plasmonic nanostructures, including nanotriangles,[18] nanorods,[19, 20] nanodisks[21]. For example, aryl layers derived from bisthiénylbenzene diazonium salts were regioselectively grafted on gold nanotriangles under visible-light illumination (Fig. 5a), in the absence of reducing agent.[18]

Spatially selective grafting could be also achieved on colloidal gold nanorods using both iodonium and diazonium salts. Plasmon-assisted homolysis of the C–I bond of iodonium salts under excitation of longitudinal plasmon resonances resulted in the regioselective grafting of organic layers on the tips of the rods while their sides were functionalized using spontaneous diazonium salt grafting.[20] In another example, lithographic gold nanorods were irradiated by a polarized laser beam along their long axis, resulting in the preferential grafting of polyaryl layers on the nanorod tips (Fig. 5b,c).[19] Interestingly, a multi-step process using successive illuminations under perpendicular polarization directions, in the presence of two different diazonium salts, enabled the formation of multifunctional patterned layers grafted at the surface of gold nanodisks.[21]

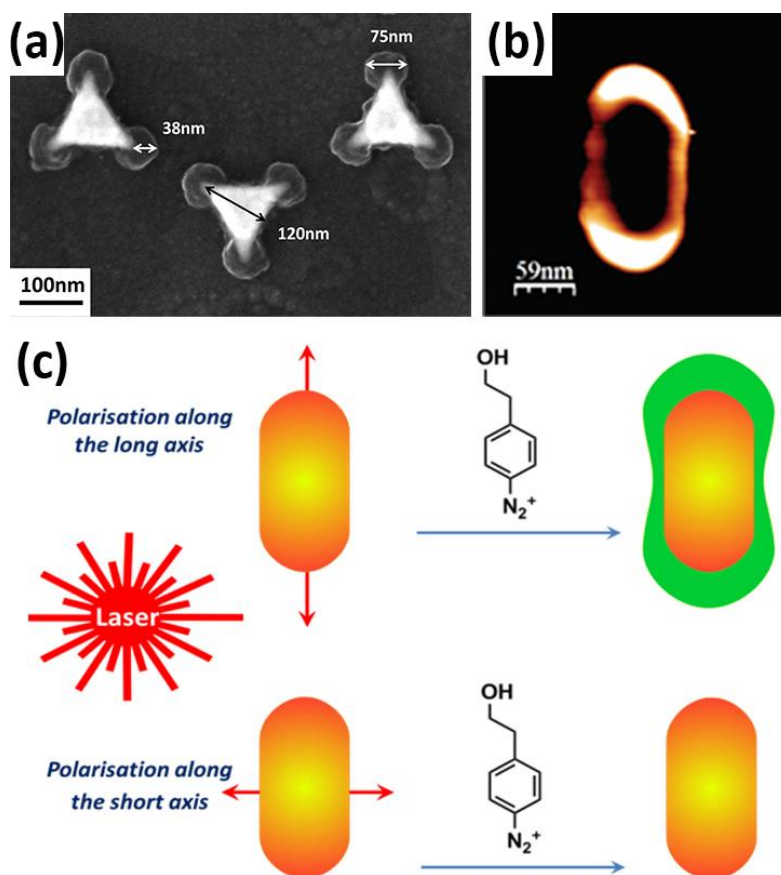


Figure 5. (a) SEM image of Au triangles after plasmon-induced grafting during 4 min under visible light irradiation, in the presence of bisthiénylbenzene diazonium salt aqueous solution; (b) Result of the difference between AFM images of Au nanorod recorded before and after plasmon-mediated grafting under illumination polarized along the long axis; (c) Representative picture of gold nanorod modified *via* regioselective surface functionalization under plasmon excitation with polarized light. (a) Reproduced and readapted with permission from ref. [18] Copyright, 2017, American Chemical Society. (b) and (c) Reproduced and readapted with permission from ref. [19]. Copyright, 2017, Royal Society of Chemistry.

4. Surface immobilization of small molecules, polymer films and biomolecules at the surface of plasmonic nanoparticles

Triggering the surface immobilization of functional species on plasmonic NPs is of great importance for advanced applications in (bio-)sensing, environment, catalysis and optics. The different strategies based on diazonium salts to attach small molecules, polymer coatings and biomolecules on the surface of metallic NPs are summarized below (Fig. 6).

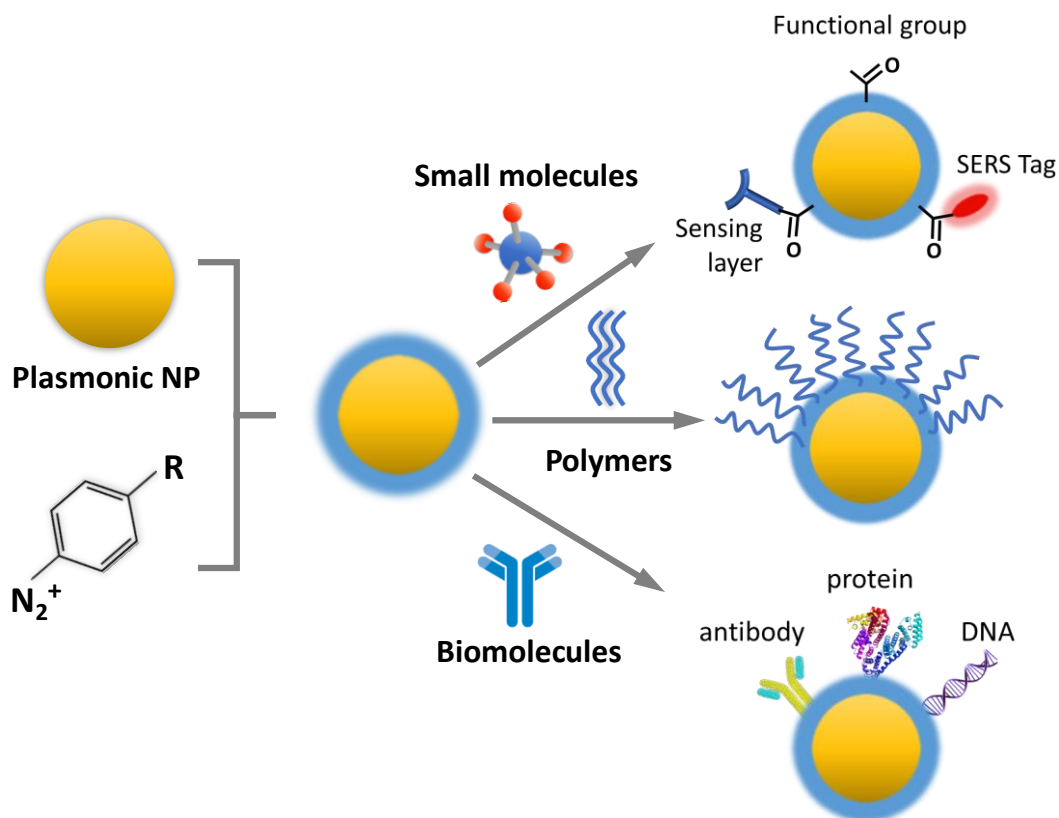


Figure 6. Representative scheme of the surface immobilization of small molecules, polymer layers and biomolecules at the surface of plasmonic NPs, *via* diazonium salt chemistry.

4.1. Surface immobilization of small molecules

Small molecules (with weight less than 900 daltons) based on aryl diazonium salts,[22] can be grafted onto metallic NPs *via* reduction of diazonium salts. The resulting organic mono- or multi-layers attached on the NPs have been considered as promising interfaces for various applications, such as chemical and bio-sensors or bioimaging tags. For example, macrocyclic compounds, such as calix[4]arenes bearing diazonium groups on their large rim were grafted on Au NPs.[23] Remarkably, these molecules can be decorated with various functions, such as oligo(ethylene glycol) chains providing an excellent colloidal stability to the nanohybrids. Mixtures of calixarenes could be also grafted on the NPs, with a fine control over the final surface chemical composition,

opening the way to the design of Au NPs coated with well-defined functional and post-functionalizable groups.[24] Thanks to this strategy, carboxyl groups from PEG layers were conjugated to amine-containing biomolecules such as peptide aptamers, for the detection of cancer biomarkers.[25] Regarding bioimaging applications, the grafting of Raman reporter groups at the surface of plasmonic NPs is an effective means to design SERS tags. Among the possible Raman reporter groups, nitro- and cyanophenyl moieties are particularly attractive as they display intense and characteristic Raman peaks, which can be easily detected by Raman imaging. These Raman labels were spontaneously grafted onto Au NPs for Raman imaging of tumor cells after NPs internalization.[14]

4.2. Surface immobilization of polymers

The development of strategies to obtain plasmonic NPs with surface-grafted polymers has stimulated a wide interest for potential application in (bio-)sensors [26], drug release [27] or environmental remediation. They can be classified into two main categories: (i) polymers can be “grafted to” the metallic NPs by adding a diazonium end group on the backbone of pre-formed polymer chains. For example, calix[4]arene-tetra-diazonium bearing four oligo(ethylene glycol) chains on their small rim [24] were used to functionalize Au NPs and provide them water solubility, steric stabilization and increased circulation lifetime in the blood; (ii) the polymerization can be driven “from” the surface where active species initiate the covalent polymerization. “Grafting from” polymerization techniques offer an accurate control of polymer coating thickness, homogeneity, and grafting density. Different polymerization mechanisms have been initiated from the surface of plasmonic NPs, including atom transfer radical polymerization (ATRP) [28], reversible addition/fragmentation chain transfer polymerization (RAFT) and polymerization controlled by an iniferter. Interestingly, the surface-initiated growing of stimuli-responsive (thermo- or pH-sensitive) polymer brushes, such as poly(N-isopropylacrilamide) (PNIPAM) by ATRP on plasmonic nanostructures was shown to yield active optical hybrid devices, which properties can be modified via an external stimulus.[29] Another strategy was based on plasmon-activated “from surface” RAFT controlled radical polymerization.[30] The RAFT agent was grafted on gold gratings via aryl diazonium salts and plasmon excitation was used to trigger surface-assisted growth of PNIPAM. The process appeared to be self-limited offering new prospects for the formation of ultrathin smart polymer coatings on gold nanostructures. The iniferter method from surface-grafted diazonium salts-derived initiators was exploited to immobilize molecularly imprinted polymers on gold nanorods to yield water-soluble plasmonic nanosensors[31] or on nanostructured copper surfaces to obtain anti-icing coatings.[32]

4.3. Surface immobilization of biomolecules

The flexible chemistry provided by the substituent on the aryl group offers many opportunities to immobilize on plasmonic NPs a wide range of biomolecules modified by

diazonium end groups or aryl layers for post-functionalization. For example, Au NPs bioconjugates with insulin [33] or bovine serum albumin (BSA) [34] were elaborated using aryl diazonium salt chemistry, demonstrating a high hemocompatibility with human red blood cells. Au NPs modified by aryl diazonium salts bearing carboxylic acid groups were coated with polydiallyldimethylammonium chloride,[35] a biodegradable cationic polyelectrolyte to form conjugates with deoxyribonucleic acid (DNA) and obtain non-viral gene systems. Capture antibodies, such as anti-B-type natriuretic peptide (anti-BNP), could also be immobilized on Au NPs grafted through aryl diazonium salt chemistry to obtain sandwich type immunoassays on screen printed carbon electrodes for the accurate detection of clinically relevant levels of BNP in human serum samples.[36] In another strategy, the amino groups of Au NPs modified by 4-aminothiophenol were transformed to diazonium salts in order to bind a tumor marker, the human p53 protein. The nanoconjugates were then captured on a sensor surface modified by another protein, azurin, which enables the formation of stable complexes with p53 protein. The transduction process was based on the SERS activity of Au NPs, resulting in intense SERS signals in the presence of p53 proteins in human serum, even at low concentrations (down to 500 fM).[37]

5. Targeted applications

Thanks to the outstanding properties of plasmonic NPs and their easy surface functionalization by aryl diazonium salts, a considerable scope for application research is open up, as illustrated in Fig. 7. It will take advantage of the enhanced colloidal stability of plasmonic NPs provided by functionalization with diazonium salts, robust interfacial links between the inorganic cores and the organic coatings and the wide variety of available functional groups. The targeted applications cover a broad range from i) biomedical and anti-bacterial science, ii) environmental protection, iii) forensic science and iv) catalysis.

5.1. Biomedical science

The use of plasmonic NPs in biomedical science has been the subject of intense research. In this field, the NPs must be modified with a variety of functional (bio-)molecules, such as drugs, targeting groups, chemical tags or antibacterial agents. For example, Au NPs were modified *via* aryl diazonium salts by BSA conjugates for drug delivery applications [34]. A remarkable hemocompatibility was observed after surface modification with BSA offering promising opportunities for intravenous drug delivery, as illustrated in Fig. 7a. Nanosensors based on molecularly imprinted polymers (MIPs) could be elaborated by combining aryl diazonium salts, iniferter polymerization and gold nanorods for the detection of analytes by SERS. The gold nanorods coated by MIPs layers enabled the SERS label-free detection of folic acid down to 0.1 μM concentration.[41]

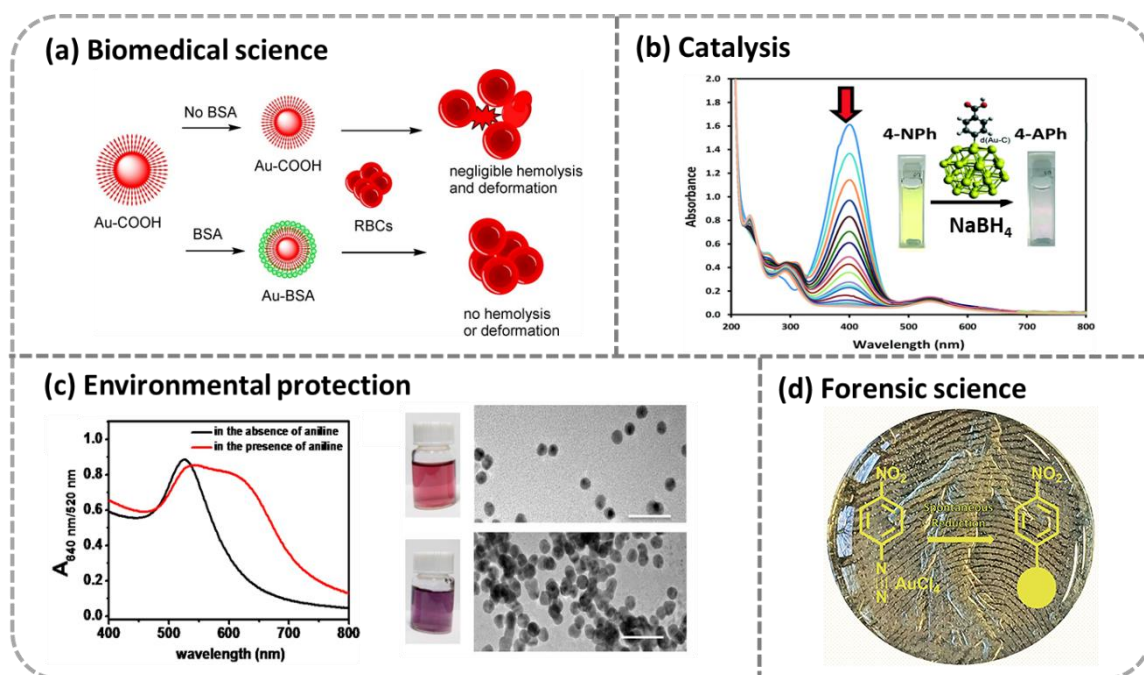


Figure 7. (a) Representative scheme of the effect of Au-BSA bioconjugates upon hemocompatibility and comparison with uncoated Au-COOH NPs. (b) UV-vis spectra recorded during the reduction of 4-NPh with NaBH_4 in the presence of AuNPs-COOH. The inset shows photos of the solution during the reduction reaction from 0 to 5 min. (c) UV-vis spectra (left) and photos (center) of Au NPs functionalized by diazonium salts, in the absence (top) and presence (bottom) of aniline ($100 \mu\text{M}$). TEM images of the corresponding Au NPs solutions in the absence (up) and the presence (down) of aniline ($100 \mu\text{M}$). Scale bars: 50 nm. (d) Latent fingerprint image obtained using diazonium solution on a nickel coin. (a) Reproduced and readapted with permission from ref. [34]. Copyright, 2018, Elsevier. (b) Reproduced and readapted with permission from ref. [38]. Copyright, 2019, Royal Society of Chemistry. (c) Reproduced and readapted with permission from ref. [39]. Copyright, 2017, Elsevier. (d) Reproduced and readapted with permission from ref.[40]. Copyright, 2021, Wiley.

Optical transduction based on SERS was also reported for the detection of p53 proteins in human serum at low concentrations[37]. In another approach, Au NPs were trapped within nanocomposite films of MIPs deposited on gold electrodes.[42] For this, immobilized Au NPs were functionalized with benzophenone, *via* aryl diazonium salts, to initiate the photopolymerization of methacrylic acid and ethylene glycol dimethacrylate, in the presence of dopamine, used as the template molecule. The resulting nanocomposite layers were used for the electrochemical label-free detection of dopamine, down to 0.35 nM concentration. Regarding antimicrobial applications, silver NPs were mainly used for their capacity to release Ag^+ ions, demonstrating strong antibacterial properties. Nevertheless, Ag NPs suffer from colloidal instability and tend to aggregate in aqueous solutions, thereby affecting their antibacterial effect. Aryl diazonium salt chemistry was exploited to improve their colloidal stability by introducing surface-grafted

carboxylic groups acting as water-soluble stabilizers, resulting in efficient antibacterial nanohybrids towards *S. Aureus*. [43]

5.2. Environmental protection

Nanocomposites were elaborated from the electrochemical reduction of [HOOC-4-C₆H₄N≡N]AuCl₄ salts in the presence of polyaniline (PANI) emeraldine salt for the removal of synthetic dyes in textile wastewater treatment. The composites were shown to exhibit a high removal rate of methylene blue dye onto nanosand paving the way towards environmental remediation applications.[44] Diazonium salts and Au NPs were also used as building blocks for the preparation of hybrid thin films on indium tin oxide (ITO) electrodes to obtain heavy metal sensors. Square wave voltammetry (SWV) measurements showed a high sensitivity for the electrochemical detection of Cu²⁺ ions, with a linear behavior between mM to pM concentrations and a detection limit of about 1 pM.[45] In another example, diazonium salt-decorated Au NPs were used to detect aniline, an important raw material in many industries, which presence in waters raises pollution concerns. The presence of aniline resulted in a fast and visible red-to-blue color change of the Au NPs solutions (Fig. 7c) allowing naked-eyes detection of arylamine-polluted water and quantitative measurements by absorbance changes.[39]

5.3. Forensic science

Diazonium salts combined with metallic NPs were evaluated as innovative developers for latent fingerprints on crime tools.[46][40] This strategy, based on the in situ reduction of aryldiazonium [4-NO₂-C₆H₄N₂]⁺AuCl₄ by the components of human sweat, allowed the formation of gold deposits on eccrine secretions present at the surface of copper, lead, nickel and aluminum surfaces. The gold deposits appeared efficient to visualize the primary, secondary, and tertiary details of the developed fingerprints. This approach was combined to the XPS technique,[47] a surface-sensitive technique for chemical analysis. The formation of robust gold-aryl films from simultaneous reduction of diazonium moieties and gold(III) in [AuCl₄]⁻ resulted in an increased gold(0) quantity on the surface of copper coins and model flat sheets. Diazonium gold(III) salts thus provide a promising alternative to common methods for latent fingerprint detection and development.

5.4. Catalysis

Water-soluble polyaryl-coated Au NPs were used as catalysts for the reduction of an environmental pollutant, 4-nitrophenol (Fig. 7b). It is noteworthy that nitrophenols are toxic organic pollutants widely spread in industrial and agricultural waste waters. Nanohybrids elaborated from the mild reduction of [HOOC-4-C₆H₄N≡N]AuCl₄ displayed high catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride.[38] A series of para-substituted phenyl groups (-CH₃, -F, -Cl, -OCF₃, and -CF₃) derived from diazonium salts were successfully grafted on the surface of Pt NPs, by co-reduction of diazonium salts and H₂PtCl₄. [48] -CF₃ functionalized Pt

NPs were shown to display the highest catalytic activity for oxygen reduction reactions (ORR), with ~ 3 times higher ORR specific activity than the value found for commercial Pt/C catalysts. In another example, palladium NP-cored G1 dendrimers obtained from the reduction of Pd^{II} in the presence of diazodendrons were used for the chemoselective room temperature hydrogenation catalysis of carbon–carbon multiple bonds, with good recyclability and short reaction times.[49] The Pd-G1 nano hybrids appeared to be also efficient catalysts for Suzuki, Stille and Hiyama coupling reactions.[50]

Table 1 summarizes the main characteristics of the various plasmonic nanomaterials functionalized by aryl diazonium salts described in this review, and their targeted applications.

Table 1. Summary of plasmonic NPs functionalized by aryl diazonium salts and their targeted applications.

Type of NPs	Shape of NPs	Functional groups on aryl rings	Immobilized objects	Targeted application	Ref.
Au	sphere	-NO ₂ , -CN, -COOH	Aryl mono- or multi-layers	SERS tags for cell labeling	[14]
Au	sphere	-C ₈ F ₁₇	Polyaryls	-	[17]
Au	sphere	-Br	PNIPAM brushes	optical sensors	[28]
Au	nanorod	-O-CH ₂ -CH ₂ -DEDTC	Molecularly imprinted polymers	Capture and detection of FA by SERS	[31]
Au	nanorod	-C ₂ H ₄ OH	Polyaryls	Regioselective grafting for nano-optics	[19]
Au	nanodisk	-COOH, -C ₂ H ₄ OH	Polyaryls		[21]
Au	nanotriangle	-BTB	Polyaryls	Plasmonic electrochemistry	[18]
Ag	spheroid	-COOH	Polyaryls	Antimicrobial applications	[43]
Pt	sphere	-CH ₃ , -F, -Cl, -OCF ₃ , -CF ₃ ,	Polyaryls	Electrocatalysis for oxygen reduction reactions	[48]
Pd	sphere	dendron	G ₁ -dendrimer	Chemoselective hydrogenation catalyst	[49]

6. Conclusion

This book chapter provides a general overview of the various surface modification strategies based on aryl diazonium salts for the functionalization of plasmonic nanomaterials. Aryl diazonium salts appear as a valuable alternative to commonly used thiol self-assembled monolayers for the modification of plasmonic nanoparticles. Indeed, they offer added-value characteristics such as (i) friendly synthesis and surface grafting protocols, (ii) broad choice of available terminal groups, (iii) robust covalent surface-C interfacial bonds and (iv) formation of multifunctional layers. Owing to these outstanding properties, surface agents based on aryl diazonium salts were applied to the functionalization of plasmonic NPs for a wide range of applications, including nanosensors, nano-optics, bioimaging, latent fingerprints, environment and antimicrobial materials.

However, this research area is still on an early stage with respect to real-life applications and several challenges need to be addressed to promote industrial development. From a methodological point of view, the mechanisms of covalent binding on the plasmonic NP surface and formation of polyaryl multilayers should be fully elucidated to achieve well-controlled nano-hybrids. In practical terms, the long-term stability of the modified nanomaterials in various environments and upon external stimulations, such as light, temperature or pH should be examined in depth. From a toxicological standpoint, the biosafety of plasmonic NPs functionalized by diazonium salts should be assessed. To tackle these issues and boost the technology transfer of diazonium salt chemistry for plasmonic NPs functionalization, it will be crucial to establish coordinated and collaborative investigations covering chemical, toxicological and industrial aspects.

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