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Active molecular plasmonics: tuning surface plasmon resonances by exploiting molecular dimensions

DOI 10.1515/nanoph-2015-0007

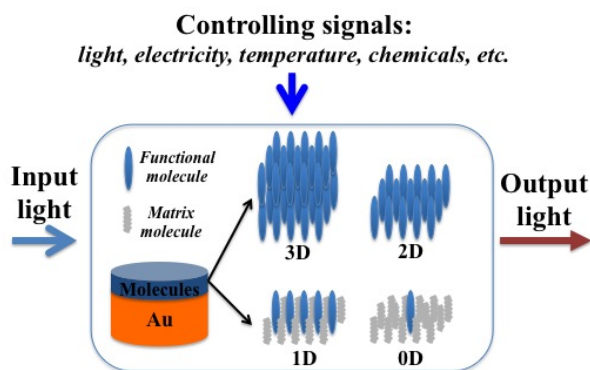
Received October 2, 2014; accepted May 1, 2015

Abstract: Molecular plasmonics explores and exploits the molecule–plasmon interactions on metal nanostructures to harness light at the nanoscale for nanophotonic spectroscopy and devices. With the functional molecules and polymers that change their structural, electrical, and/or optical properties in response to external stimuli such as electric fields and light, one can dynamically tune the plasmonic properties for enhanced or new applications, leading to a new research area known as active molecular plasmonics (AMP). Recent progress in molecular design, tailored synthesis, and self-assembly has enabled a variety of scenarios of plasmonic tuning for a broad range of AMP applications. Dimension (i.e., zero-, two-, and three-dimensional) of the molecules on metal nanostructures has proved to be an effective indicator for defining the specific scenarios. In this review article, we focus on structuring the field of AMP based on the dimension of molecules and discussing the state of the art of AMP. Our perspective on the upcoming challenges and opportunities in the emerging field of AMP is also included.

plasmon–molecule interactions, polymers, surface plasmons

1 Introduction

Plasmonics, a burgeoning branch of photonics, has been attracting extensive attention across various fields over the past two decades [1–3]. The core of this field lies in the surface-plasmon-enabled manipulation of light–matter interactions at the nanoscale [4–6]. With their capability of concentrating and transporting light at the nanoscale, surface plasmons (SPs), which are the light-coupled coherent oscillations of free electrons confined at the interfaces of nanostructured metals (or doped semi-



Keywords: active molecular plasmonics, dimension, graphene, molecular switches, organic materials,

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conductors) and dielectric materials, have opened up a new window of opportunities for applications in nanophotonic integrated circuits [7–13], surface-enhanced optical spectroscopy [14–16], energy harvesting [17–19], and super-resolution optical imaging [20, 21]. Advancements in transformation optics and nanofabrication techniques (both “top-down” lithography and “bottom-up” chemical synthesis/self-assembly) have also boosted many other applications associated with the intriguing properties of plasmonic metamaterials [22–28]. While some of the applications can be fully accomplished with passive plasmonic nanostructures that exhibit constant optical response, it requires reconfigurable or tunable SPs, which is known as active plasmonics [29], to develop other applications such as plasmonic switches [30–33], plasmonic modulators [34, 35], and tunable color filters [36, 37].

Due to the high sensitivity of SPs to the optical properties of dielectric materials surrounding the plasmonic nanostructures [38, 39], use of tunable dielectric materials has proved to be an effective approach towards active plasmonics [40, 41]. In particular, functional molecules and organic materials exhibit multiple advantages for the active plasmonic applications [42–44]. First, the responsive properties of organic materials to external stimuli can be precisely modified down to the atomic level for a broad range of tunability of SPs to meet the requirements of variable applications. Second, due to their small size, molecules provide the ultimate miniaturization of active nanostructures and devices. Third, the applicability of self-assembly of molecules enables the low-cost, high-throughput fabrication of materials and devices. Finally, softness and biocompatibility of organic materials facilitates the development of flexible optical materials and devices for biomedical applications.

These advantages of organic molecules and materials have led to the rapid development of a subfield known as active molecular plasmonics (AMP) [43]. One of the primary principles of AMP is to harness the externally controllable changes in the structural, electrical, and/or dielectric properties of organic materials for the dynamic tuning of SPs in terms of resonance wavelength, phase and/or amplitude, which is also the subject of this review. So far, a wide range of organic materials, including simple molecules, supramolecules, macromolecules, and polymers, has enabled AMP with various device configurations and applications [45–51]. It is noted that there is another important constituent part in the field of AMP, which involves the synergistic integration of plasmonic nanostructures with active gain media, such as dye molecules [52–55]. This subfield focuses on compensating the inherent ohmic loss in the metal with molecular gain systems and

is the key for the development of plasmonic lasers. Excellent review about this subfield can be found in [55, 56]. In this review, we focus on the SP-tuning mechanisms that exploit the dimensions of functional molecules and the phrase “AMP” is therefore used for this reference unless stated otherwise.

A review article that intends to structure the emerging field of AMP will be extremely helpful in guiding those who are new to this field, revealing current limitations and challenges, and directing future research efforts. Due to its highly interdisciplinary nature, the field of AMP can be categorized based on many different parameters such as external stimuli, organic materials, and plasmonic nanostructures. Herein, we argue that the dimension of molecules is standing out as an effective parameter in structuring the field of AMP due to its critical role in defining different tuning scenarios of SPs by functional molecules. In particular, the dimension of molecules can significantly impact the tunability of SPs through controlling the strength of plasmon–molecule interactions, the changes of optical properties of molecules, the density of molecules, and their switchability. In the following, we use representative examples to illustrate the working principle of AMP, which is categorized according to the dimension of functional molecules and materials on metal nanostructures, that is, three-dimensional (3D), two-dimensional (2D), and zero-dimensional (0D).

2 Three-Dimensional Organic Materials

In the context of AMP, we define 3D organic materials as those with all the dimensions larger than the skin depth of SPs on plasmonic nanostructures. Since SPs exist at the near field of the nanostructures with a subwavelength skin depth in dielectric materials, 3D organic materials interact with a whole field of SPs [57–67]. As a result, the AMP performances based on 3D organic materials largely depend on the materials’ switchability and tunability in the optical properties, as well as the sensitivity of plasmonic nanostructures. Common 3D organic materials for AMP include liquid crystals (LCs) and responsive polymers.

2.1 Liquid Crystals

LCs have several phases with long-range periodic order in 3D such as nematic, smectic, and cholesteric. Controlling the phases with external stimuli (e.g., electricity, light, and

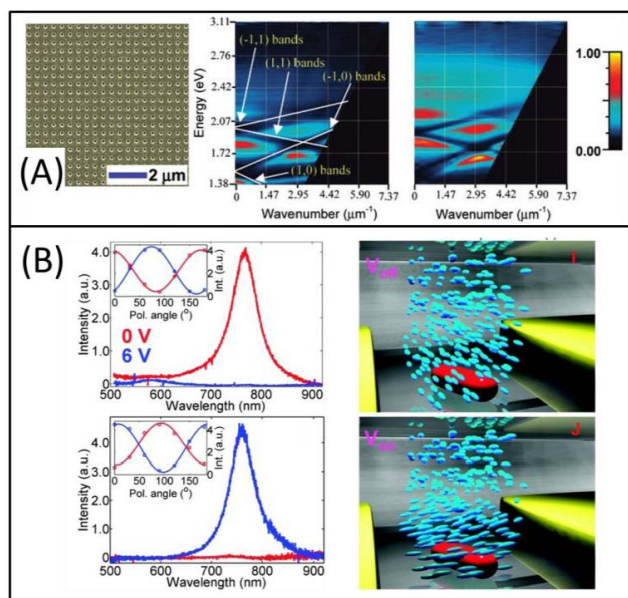


Figure 1: (A) LC-based electrical tuning of optical transmission through 2D nanohole arrays within metal thin films. From left to right: SEM image of nanohole arrays, and optical transmission dispersion plots without (middle) and with (right) application of electric field. LC: liquid crystal. (B) 100% on/off electrical switching of scattering of polarized light by hybrid structures of LCs and Au nanorods. Left column: optical scattering spectra of the hybrid structures with Au nanorods parallel (top) and perpendicular (right) to the polarizer upon the application of different voltages (red spectra: 0 V and blue spectra: 6 V). Insets show the dependence of the intensity of scattering resonant peaks on the polarizer angle. Right column: schematic illustration of LC-nanorod hybrid structures with and without application of switching voltage. Panel (A) adapted from Ref. [57] with permission. Copyright (2008) American Chemical Society. Panel (B) adapted from Ref. [58] with permission. Copyright (2011) American Chemical Society.

acoustic waves) tunes the optical properties of LCs. For example, nematic LCs that have a uniform alignment of the director exhibit uniaxial optical symmetry with two principal refractive indices, that is, ordinary refractive index n_o and extraordinary refractive index n_e [68]. Stimulus-induced changes in the orientation of the director cause changes in the refractive index experienced by the incident light. Because of their switchable optical property and mature technology, LCs have been broadly applied to the field of AMP [69–78]. A couple of examples are given below to illustrate the working principles based on different metal nanostructures and external stimuli.

Dickson and colleagues have demonstrated electrically tunable SPs and the associated extraordinary optical transmission through 1D and 2D metallic nanohole arrays covered by LCs [57]. As shown in Figure 1A, the optical transmission dispersion is reversibly switchable by elec-

trical control of the phase of LCs, leading to the electrical tuning of both intensity and peak wavelength of the maximally transmitted light. The tuning is enabled by the phase transition of LCs that causes the changes in the refractive index of LCs experienced by the SPs.

Using different types of metal nanostructures, one can change the LC-based AMP scenarios. For example, Khatua *et al.* have realized a 100% on/off switching of light scattering based on hybrid structures of LCs and Au nanorods [58]. As shown in Figure 1B, application of electric field to the hybrid structures leads to a phase transition of LCs from “homogeneous nematic” (voltage off) to “twisted nematic” (voltage on). Due to the large birefringence, the twisted nematic LCs cause an orthogonal rotation of the plasmon-enhanced scattering light from the Au nanorods. When properly polarized incident light is used, a 100% modulation in the scattered light with a switching time of tens of milliseconds can be achieved using a voltage as low as 4 V. Other LC-based AMP applications include directional fluorescence [79], tunable metamaterials [80–82], and tunable lenses [83].

The capability of tailoring LCs to be responsive to other stimuli such as light [84–87], acoustic wave [88], and heat [89] has offered great flexibility on the selection of activation methods for AMP. For example, LCs doped with azobenzene that undergoes *trans-cis* photoisomerization become photoswitchable [84]. The photoswitchable LCs have been employed to reversibly modulate the localized surface plasmon resonances (LSPRs) of Au nanoparticles.

2.2 Responsive Polymers

Responsive polymers are another type of widely used 3D organic materials in AMP. Different functional groups, which are responsive to heat, light, electricity, or chemical, can be readily grafted to the polymer chains to enable the switching of polymer properties with external stimuli. Responsive polymers can also be achieved by incorporating molecular switches (e.g., azobenzene and spiropyran) within otherwise passive polymers in a host-guest format. The AMP examples given below cover both types of responsive polymers.

Poly(N-isopropylacrylamide) (PNIPAM) is one of the commonly studied responsive polymers, which undergoes heat-induced phase transition between hydrophilic swelling state and hydrophobic shrinking state [90]. The phase transition has been harnessed for AMP through the changes in refractive index of the polymers and/or interparticle coupling [59–64]. As demonstrated by Mitsuishi and colleagues (Figure 2A), Au nanoparticles embedded in

PNIPAM brushes exhibit thermally controllable peak shifts in the LSPRs due to a refractive index change caused by the phase transition of the polymers [59]. In another experiment with PNIPAM microgels coated with polyelectrolyte-modified Au nanorods, as shown in Figure 2B, the phase transition induced changes in the size (which, in turn, affects the coupling between the nanorods), and refractive index of the microgels, thus resulting in the peak shifts of LSPRs of the nanorods [63]. The capability of PNIPAM in tuning SPs has also been harnessed for the dynamic surface-enhanced Raman spectroscopy (SERS) substrates. As shown in Figure 2C, the phase transition of PNIPAM sandwiched between Au nanospheres and Au thin films tunes the plasmonic coupling and thus, the Raman enhancement of probe molecules [64]. Hybrid systems using other types of thermoresponsive polymers have also been demonstrated [65, 66].

An alternative approach towards responsive polymers is to incorporate molecular switches within otherwise passive polymers in a host-guest format. This approach takes advantages of a broad range of molecular switches, which changes their structural and optical properties in response to external stimuli, to enrich the variety of responsive polymers for AMP [49, 50, 67]. For example, Zheng *et al.* employed photoresponsive polymers, which consist of poly(methyl methacrylate) (PMMA) doped with spiropyran, to study the switchable plasmon–exciton coupling [67]. The spiropyran molecules in PMMA retain their photoisomerization and reversibly switch between their closed form to open form upon alternative irradiation of UV and visible light (Figure 3). The photoisomerization tunes the plasmon–exciton coupling between the Au nanodisks and spiropyran molecules. In other AMP applications, PMMA thin films doped with spiropyran have been used to achieve switching function in surface plasmon polariton (SPP) waveguides [50].

3 Two-Dimensional Functional Molecules

In order to develop ultra-compact AMP devices, 2D functional molecules are preferred for the active tuning of SPs due to the ultra-small thickness (from several nanometer to atomic thickness). Compared with their 3D counterparts, the 2D molecules usually lead to the largely decreased plasmonic tunability since the plasmon–molecule interactions occur only within the limited regions that are usually smaller than the skin depth of SPs. However, benefiting from the maximal intensity of SPs at the surfaces

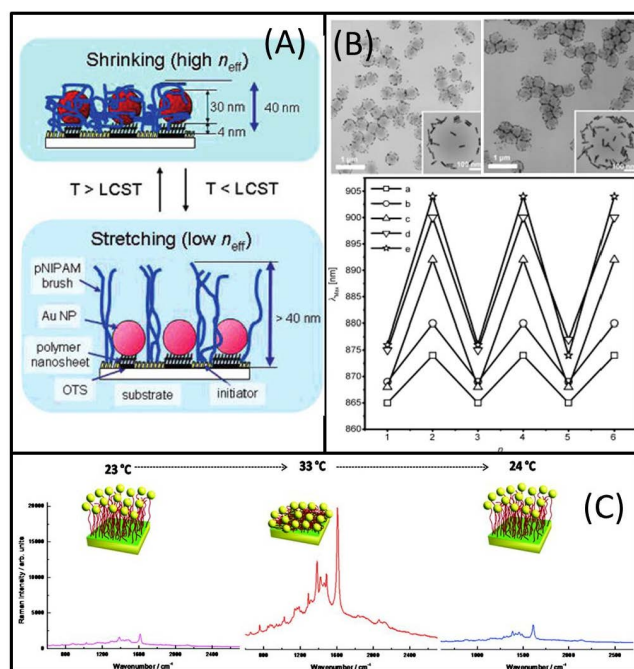


Figure 2: (A) Reversible thermal tuning of the LSPRs of Au nanospheres embedded in thermoresponsive PNIPAM brushes. Increasing the temperature passing LCST causes shrinking of the brushes leading to higher refractive index and vice versa. LSPRs: localized surface plasmon resonances; LCST: lower critical solution temperature; PNIPAM: Poly(N-isopropylacrylamide). (B) Top: TEM images of PNIPAM microgels loaded with Au nanorods with different concentrations. Bottom: Peak shifts of the LSPRs of the nanorods due to the repeated temperature changes. The Au nanorod coverage increases from samples “a” to “e”. (C) Dynamic SERS signal from Au NP-PNIPAM-Au substrate systems at various temperatures- Panel (A) adapted with permission from Ref. [59]. Copyright (2007) American Chemical Society. Panel (B) adapted with permission from Ref. [63]. Copyright 2007, Wiley. Panel (C) adapted with permission from Ref. [64]. Copyright (2010) American Chemical Society.

of plasmonic nanostructures where the 2D molecules are located, the large plasmonic tunability required for practical applications can still be achieved with the 2D configurations. As described below, two types of functional molecules, that is, self-assembled monolayers (SAMs) of molecular switches and graphene, exhibit great potential for the 2D AMP.

3.1 Self-Assembled Monolayers of Molecular Switches

With proper surface chemistry, molecular switches can form 2D SAMs on the surfaces of plasmonic nanostructures. For instance, molecular switches can be functionalized with thiol groups to form SAMs on the surfaces of Au

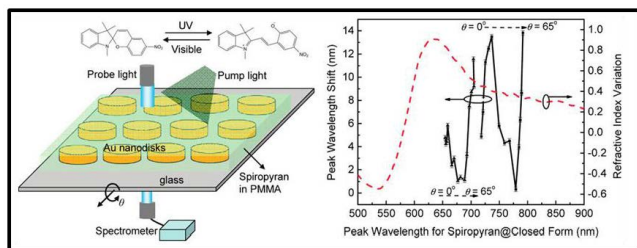


Figure 3: Left: Schematic illustrations of the hybrid structures of Au nanodisk arrays covered by PMMA doped with spiropyran molecules and the experimental setup for the angle-resolved optical transmission measurements. Right: The dispersion curve of the peak shift as a function of the peak wavelength of the LSPRs with the spiropyran in its closed form. Also included is the curve for the isomerization-induced refractive index variation of the molecules. Adapted with permission from Ref. [67]. Copyright (2011) American Chemical Society. PMMA: poly(methyl methacrylate); LSPRs: localized surface plasmon resonances.

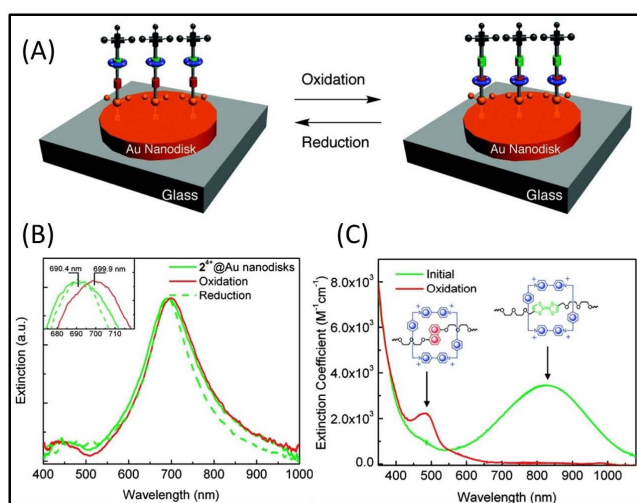


Figure 4: (A) Schematic illustration of the redox control of the SAMs of rotaxane molecules tuning the LSPRs of Au nanodisk. SAMs: self-assembled monolayers; LSPRs: localized surface plasmon resonances. (B) Extinction optical spectra of the rotaxane-attached Au nanodisks revealing the peak shift in the LSPRs upon redox control of the rotaxane. Inset is an expanded view around the peak maxima in the spectra. (C) Extinction optical spectra of rotaxane in solution before and after oxidation. The chemical structures indicate the ring position within the dumbbell structure. Adapted with permission from Ref. [43]. Copyright (2009) American Chemical Society.

and Ag nanostructures, which are the common plasmonic materials. Typically, the SAMs have a thickness of several nanometers, leading to the ultra-compact and highly integrated AMP devices. In addition, the self-assembly process enables the low-cost and high-throughput fabrication of AMP structures of both 2D and 3D configurations.

As an example, Zheng and colleagues demonstrated AMP based on Au nanodisks covered with SAMs of bistable

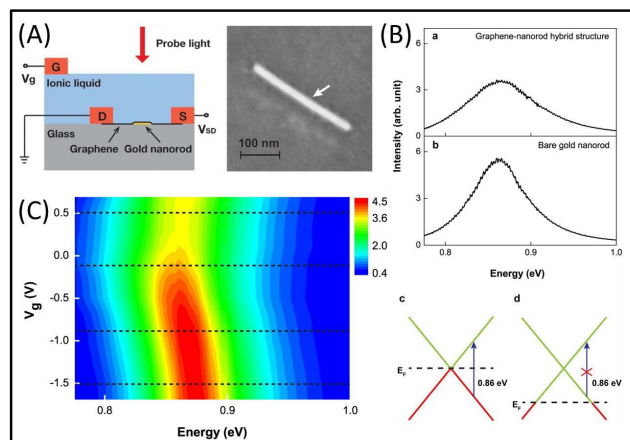


Figure 5: (A) Schematic and SEM image of the tunable graphene-Au nanorod hybrid system. (B) (a&b) show that optical absorption in graphene broadens the bandwidth of LSPRs. (c&d) illustrate the effects of Fermi level E_f on the optical absorption of graphene. (C) 2D mapping of optical spectra of the gated graphene-Au nanorod system revealing the effects of gating voltage V_g on the peak wavelength and intensity of the LSPRs. Adapted with permission from Ref. [103]. Copyright (2012) American Chemical Society. LSPRs: localized surface plasmon resonances.

rotaxanes [43]. Rotaxane is a mechanically interlocked molecular architecture consisting of a “dumbbell-shaped molecule” that is threaded through a “macrocyclic ring.” The ring can be controlled at two different stations within the dumbbell based on redox process. As shown in Figure 4A, the reversible and controllable mechanical motions of rings in rotaxane molecules that are exposed alternatively to oxidant or reductant tune the LSPRs of the nanodisks. Based on the redox switching of the SAMs of rotaxane (< 10 nm in thickness), reversible peak shift of ~ 10 nm in the LSPRs was observed (Figure 4B). Both experimental measurements of molecular absorption and microscopic calculations based on density functional theory reveals that the redox-induced ring shuttling causes a change in the polarization of the rotaxane, which accounts for the difference in the refractive index between the two states of the SAMs.

3.2 Graphene

Graphene, a truly 2D sheet of hexagonally arranged carbon atoms [91], has demonstrated widely tunable optical properties for its use in the ultra-thin AMP devices [92–97]. In most cases, the tunability of graphene is realized with electrostatic gating, which modifies the optical sur-

face conductivity $\sigma(\omega)$ of the graphene via [94]

$$\sigma(\omega) = \frac{ie^2}{\pi\hbar} \left\{ \frac{E_F}{\hbar(\omega + i\gamma)} \right\} + \frac{ie^2}{4\pi\hbar} \left\{ \ln \left| \frac{\hbar\omega - 2E_F}{\hbar\omega + 2E_F} \right| - i\pi\theta(\hbar\omega - 2E_F) \right\} \quad (1)$$

where E_F is the Fermi energy, which can be tuned with gating, and γ is the collision frequency. The first and second terms come from the intraband and interband transition in the graphene, respectively. The contribution of each term varies in different wavelength range. Since the optical conductivity is related to the graphene permittivity: $\varepsilon = 1 + i\sigma(\omega)/\omega\varepsilon_0t_G$, where t_G is the thickness of the graphene, it is possible to modulate the surface plasmon resonances of plasmonic nanoparticles with electrostatic gating of the graphene. In addition, due to the free carriers, graphene itself can support SPs, which can be tuned by electrostatic gating with the same mechanism [98–102]. In the following, we discuss in detail AMP where graphene is used as active dielectric media.

When graphene is used as active dielectric media, AMP is based on hybrid structures that consist of graphene and metal nanostructures. The tunability of the optical response from the hybrid structures depends on the gating-induced changes in both optical absorption of graphene and SPs in metal nanostructures. For example, Kim *et al.* demonstrated the active tuning in a hybrid graphene–Au nanorod system where a single-layer graphene covers a single Au nanorod (Figure 5A) [103]. The tuning is attributed to the gating-induced changes in both optical absorption and carrier density of graphene. The optical absorption, which arises from the interband transition, is determined by the Fermi level E_F of graphene that depends on the gating voltage (referring to c&d in Figure 5B). The optical absorption increases the FWHM (full-width-half-maximum) of LSPRs of the nanorods (Figure 5B). Meanwhile, the carrier density affects the FWHM, peak wavelength, and the intensity of LSPRs of the nanorods (Figure 5C). In a similar fashion, graphene-based tuning has been applied to other plasmonic nanostructures such as bowtie nanoantennas [104] and end-to-end nanoantenna arrays [105]. In addition, nanostructures with exquisite designs can give rise to Fano resonances [106–109], which can enhance the light–graphene interaction and lead to more efficient electrical modulation [96, 97].

4 Zero-Dimensional Functional Molecules

Due to the physical hindrance and surface quenching, the switching efficiency and kinetics of SAMs of molecular switches on metal surfaces are significantly decreased, limiting the modulation depth and switching time in AMP. Isolating single molecular switches within the well-defined SAMs of structural molecules as matrices (e.g., alkanethiols) has proved to be an effective approach towards reducing the physical hindrance [110–115]. These isolated single molecular switches, which we refer to as OD molecules, are well separated from each other with their functional groups protruding above the SAM matrices and have very limited interactions with other molecular switches and matrix molecules, leading to the enhanced switching efficiency and kinetics. Furthermore, the SAM matrices offer the well-defined nanoenvironments for both single-molecule analysis and functional control of the molecular switches.

The performance-enhanced AMP has been demonstrated with OD azobenzene-based molecular switches [116]. Azobenzene exhibits the reversible photoisomerization between *trans* and *cis* isomers upon its alternative exposure to UV and visible light. The changes in optical properties associated with photoisomerization can tune the SPs in metal nanostructures. However, SAMs of azobenzene exhibit low isomerization efficiency due to the physical hindrance from the large contour changes of *trans*–*cis* isomerization, which has rarely been applied to AMP. By creating OD azobenzene isolated within the domains of SAMs of alkanethiols on Au nanoprisms, Joshi *et al.* demonstrated a 21 nm peak shift in the LSPRs of the nanoprisms upon the photoisomerization of azobenzene despite the low concentration of the molecular switches (Figure 6A) [116]. To achieve the maximal peak shift, the concentration of OD azobenzene in SAMs was optimized to reach a balance between the isomerization efficiency and the density of azobenzene on nanoprisms. Direct evidence of the switching efficiency and kinetics of OD azobenzene has been obtained with time-resolved SERS measurements (Figure 6B) [110].

5 Theoretical Analysis

To optimize the performance of AMP devices requires guidelines on the efficient tuning of SPs. Intuitively, one need place active molecules at sites on the plasmonic

nanostructures with the mostly enhanced field intensity in order to achieve AMP devices with the large tunability. A theoretical model helps provide more insights into the device design as well as the selection of molecules and plasmonic nanostructures. So far, the majority of the tuning mechanisms in AMP devices are based on the controllable changes in the refractive index of the materials surrounding the plasmonic nanostructures. Therefore, the similar design principle developed for the intensely studied refractive index-based plasmonic sensing can be borrowed here [117].

There are excellent works on theoretical modeling of refractive index-based plasmonic sensing [118–121]. Recently, Zhang *et al.* proposed a universal theory [122], where an equation is derived using perturbation theory to describe the resonance frequency shift of plasmonic nanostructures due to the adsorption of a dielectric sphere:

$$\Delta\omega = -\alpha_E \frac{d\omega}{d\varepsilon} |E(\vec{r}_E)|^2 \quad (2)$$

where α_E is the polarizability of the sphere, $\frac{d\omega}{d\varepsilon}$ is the material dispersion of the nanostructure, and $|E(\vec{r}_E)|^2$ is the electric field intensity at the location of the dielectric sphere. This simple linear relation is applicable to any type of dispersive nanostructures irrespective of their dimension and material as demonstrated in Figure 7.

For 3D and 2D AMP, active molecules are often distributed uniformly around the plasmonic nanostructures. For 0D systems, active molecules are scattered across the nanostructure surface. To improve the performance of AMP devices, one need maximize the resonance shift with the guidance of Eq. 2. Basically, active molecules should be confined within the plasmonic hot spots to maximize the plasmon–molecule coupling. It has been shown that selective functionalization with plasmon-activated photochemistry can be employed to achieve the site-selective control of molecules [123].

In addition, the position of functional groups within the tethered molecules also affects the coupling between the molecules and the metal. Davis *et al.* calculated the optical interactions between a point dipole and an Au nanorod using quasi-static approximation [118]. The maximal interactions exist at an optimal value of the hemisphere radius and the distance between the dipole and the Au surface. For a dipole that is 10 nm away from the end-cap of the nanorod, the maximum coupling occurs with a hemisphere radius of approximately 6 nm. This effect is consistent with the observation that plasmonic nanoparticles with sharp features such as nanostars have the higher sensitivity [124].

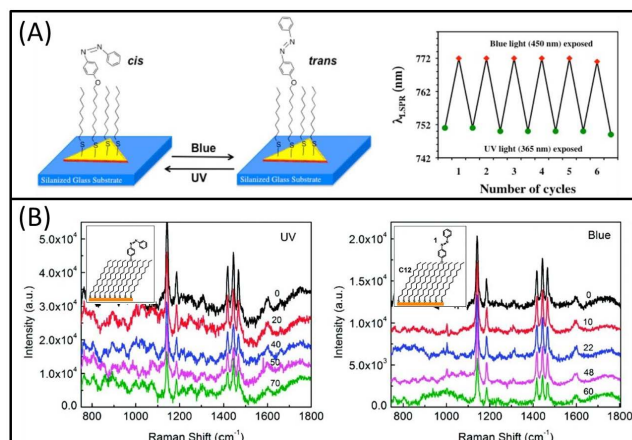


Figure 6: (A) Left: Schematic of *trans*–*cis* photoisomerization of 0D azobenzene isolated within the alkanethiolate SAMs on an Au nanoprism. Right: Reversible peak shift in the LSPRs of the 0D-azobenzene-attached Au nanoprisms upon an alternative irradiation of UV and blue light. SAMs: self-assembled monolayers; LSPRs: localized surface plasmon resonances. (B) Time-resolved SERS spectra of 0D azobenzene molecules under UV (left) and blue (right) illumination. Insets show the cross-sectional views of the 0D azobenzene in *cis* and *trans* isomers. Panel (A) adapted from Ref. [116] with permission. Copyright (2014) American Chemical Society. Panel (B) adapted from Ref. [110] with permission. Copyright (2011) American Chemical Society. SERS: surface-enhanced Raman spectroscopy.

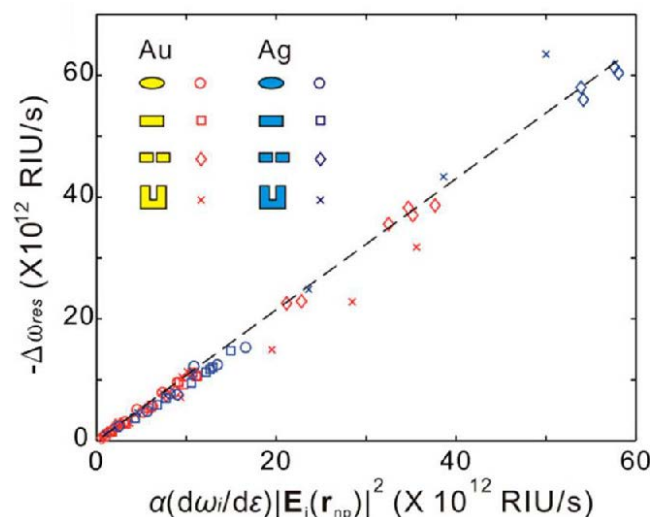


Figure 7: Implementation of Eq. 2 for four different plasmonic nanostructures made from Au and Ag. For each nanostructure, data of five different locations of the dielectric sphere (5 nm Si nanosphere) are presented. Adapted with permission from Ref. [122]. Copyright (2015) American Chemical Society.

As shown in Eq. 2, another important factor in determining the resonance frequency shift is the polarizability of the dielectric sphere. Different from bringing the di-

electric sphere to the vicinity of the plasmonic nanostructure, AMP systems usually involve the reversible change of the polarizability associated with the molecular configuration for the tuning of the plasmonic resonance frequency. Therefore, molecules with the large changes of polarizability are preferred for AMP. For azobenzene, the dipole moment of the molecule changes from almost 0D in *trans* to 3D in *cis* conformation [125]. With tailored design and chemical synthesis, one can attain active molecules with the large change of polarizability as required for practical applications [126].

Besides a large electromagnetic field enhancement, some AMP applications require plasmonic nanostructures with a narrow resonance bandwidth. The narrow bandwidth usually increases the quality factor and tunability. To this end, plasmonic nanostructures that exhibit Fano resonances offer a feasible route [106–109].

6 Conclusions and Outlook

In summary, intense research in AMP has revealed its great potential for applications in ultra-compact, high-performance nanophotonic devices and spectroscopy. Advances in molecular engineering and plasmonics have led to a wide range of AMP scenarios, which differ in architectures, external stimuli, switching speed, and modulation depth of SPs. We have discussed and structured the various AMP scenarios according to the dimension of molecules on metal nanostructures and the tuning mechanisms. Through the dimension-based categorization, we intend to provide a clear picture of the scope of AMP research and to gain new insights into current challenges and upcoming opportunities in AMP, as described below.

3D functional molecules and polymers can provide the large optical modulations through their interactions with the full field of SPs. However, the bulkiness of 3D materials hinders their potential applications in the ultra-thin and ultra-compact nanodevices. Tremendous opportunities exist in the development of new processing methods that will enable the precise control of the thickness and conformation of organic materials down to the sub-nanometer scale on metal nanostructures in order to realize the desired tunability of SPs.

2D functional molecules have paved the way towards the ultra-thin AMP devices. Graphene with a single atomic layer not only represents the ultimate miniaturization, but also enables a large signal modulation due to the capability of electrostatic gating in significantly changing its carrier density. However, the reproducibility and predictabil-

ity performance of graphene-based AMP will require the atomic-level control at the interfaces between graphene and metal nanostructures, which has rarely been demonstrated.

2D SAMs of molecular switches enable the precise control of the molecule–metal interfaces through surface chemistry. Moreover, the self-assembly process leads to the conformational coating of molecular switches on metal nanostructures of an arbitrary architecture. However, challenges with the 2D SAMs of molecular switches arise from physical hindrance and surface quenching of excited molecules on metal surfaces, which reduces the modulation depth and speed of SPs due to the decreased switching efficiency and kinetics of molecules. Much more work needs to be done to design and control intermolecular and molecule–substrate interactions in 2D SAMs of molecular switches on metal surfaces (both atomic-flat and curved surfaces [112]) in order to achieve high switching efficiency while maintaining high density of molecules.

0D functional molecules can significantly reduce the physical hindrance in the 2D SAMs of molecular switches by isolating the single molecules within the well-defined matrices. However, there is a tradeoff between the increased switching efficiency and the decreased molecular density for the 0D molecular switches. Beyond practical applications, 0D molecules provide an ideal platform for the fundamental studies of molecular switches on metal surfaces since they allow for the separation of intermolecular and molecule–substrate interactions and the evaluation of the effects of each on the switching behaviors. The well-defined matrices also provide reference background for the single-molecule measurements. Such fundamental studies will lead to new knowledge for the rational design of high-efficient molecular switches on metal surfaces that enable the high-speed and large-depth modulation of SPs.

Non-uniformity of SPs on metal nanostructure presents additional challenges and opportunities for all types of dimensions of AMP. There are plasmonic hot spots with the highest intensity of SPs in metal nanostructures, which are most sensitive to the environments. To maximize the modulation depth of SPs, functional molecules need to be confined within the “hot spots.” Progress in directed and selective assembly will pave the way towards precisely positioning molecules in these hot spots.

Critical to address some of the challenges in AMP is the development of advanced analytical tools. Specifically, new tools that enable simultaneous measurements of structures, dynamics, and functions of molecules and polymers at the single-molecule and single-nanoparticle levels will be of great help to better understand the plasmon–molecule interactions. Tremendous efforts have

been made in developing such tools by integrating optical spectroscopy with scanning probe microscopy. The former provides the chemical identity of molecules while the latter enables the atomic-scale imaging. These tools are also being expanded to be applicable to both atomic-flat and curved surfaces that are ubiquitous in metal nanostructures. Moreover, nanofabrication techniques ranging from “top-down” lithography to “bottom-up” assembly to hybrid approaches must be advanced to enable the high-throughput, low-cost production of the hybrid nanosystems of plasmonic nanostructures and molecules with the increased complexity and controllability. AMP is truly a multidisciplinary field with tremendous opportunities for both fundamental studies and engineering applications, and its advancement in multiple dimensions requires coordinated efforts from researchers with different backgrounds, including physics, chemistry, materials science, and engineering.

Acknowledgement: Y. B. Z. acknowledges financial support from the startup grant from Cockrell School of Engineering at the University of Texas at Austin and the Beckman Young Investigator Program. E. S. P. L and Y. J. L. acknowledge financial support from Agency for Science, Technology and Research (A*STAR), under the grant No. 12302FG012, 0921540098, and 0921540099.

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