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# Optical Response of Nanostructures: From Pure to Alloyed Metals

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### 5.1 Introduction

The optical properties of metals on the nanoscale differ drastically when compared with their bulk materials. In particular, collective excitations of the conduction electrons in metals under exposure to electromagnetic radiation form propagating surface waves known as surface plasmon polaritons (SPPs) in metal thin films and coherent oscillations known as localized surface plasmon resonance (LSPR) in nanostructures; see Fig. 5.1. In the first case, the SPP travels along a metal/dielectric interface with exponentially decaying electric fields  $(E_z)$  normal to the surface, as presented in Fig. 5.1A. For localized plasmon resonance, incident radiation (Fig. 5.1B) couples directly to the electrons in the metal, and dipole oscillations (labeled as + and -) arise in the nanoparticles (NPs) that result in extremely high electric fields close to the surface of the NP and resonantly enhanced scattering and absorption. Consequently, both cases lead to high confinement of the photon density at scales much smaller than their wavelength [1], which is useful for a wide variety of applications including waveguiding, sensing, energy harvesting, perfect absorption, optoelectronics, electrocatalysis, and photothermal therapy [2–6]. Depending on the specific application, precise control of the properties of the SPP and LSPR is necessary to achieve superior performance for photonic devices.

Extensive studies indicate that the resonances of nanoscale systems heavily depend on the sizes and shapes of the relevant components [7–9]. Strong contrast between the dielectric functions of the metal and the surrounding material also provides a significant impact on the wavelength and intensity of the LSPR excitation. Moreover, as will be discussed in this chapter, it has recently been reported that varying the relative composition of the metals by alloying has proved to be an effective method to tune the dielectric function and therefore the optical characteristics of a material [10–12]. Another way to tailor the resonant properties is to use ordered arrangements of two or more nanoparticles (NPs) [13]. When NPs are brought into close proximity, new collective responses are achieved that strongly depend on their geometric arrangement.



**FIG. 5.1** (A) Cross-sectional schematic of SPP propagation at a metal/air interface.  $E_x$  and  $E_z$  are the electric field components along x and z direction, respectively.  $\lambda_{spp}$  is the wavelength of the surface plasmon wave.  $\varepsilon_d$  and  $\varepsilon_m$  is the permittivity of the dielectric and the metal, respectively, and is the frequency of the incident light. (B) Illustration of LSPR excitation in a metallic nanoparticle as a function of time (t). Here, the incident radiation induces a dipole oscillation of the electrons in the metal sphere.

Typically, precise control of the nanostructures' geometry is obtained via bottom-up methods. For instance, electron-beam lithography provides exquisite control of the size, shape, and distribution of NPs in nanoscale systems, as will be discussed in Section 5.3. This fabrication process has enabled novel optical phenomenon such as Fano resonance [14,15]. Nevertheless, its scalability is severely limited by the cost and the time required to obtain large-area arrays, which limits its practical applications. To overcome the constraint of bottom-up nanofabrication, chemistry techniques have been developed that enable the formation of self-assembled nanostructures, where the final size and geometry of the building blocks are primarily determined by the precursors and the synthesis parameters [16]. Specifically, the use of block copolymers (BCPs) to facilitate selfassembly has become an attractive method in nanofabrication. BCPs have a well-controlled length and size, making them an enticing candidate for realizing scalable systems formed by nanostructures [16-18]. This approach allows for good control of the geometric arrangement, can be dispersed as an adaptable coating, and results in reduced optical losses due to the crystalline structure of the colloid [3,13,19,20]. Moreover, utilizing self-assembled structures as building blocks for large-scale, next-generation metamaterials could allow for unprecedented control of light, which has applications ranging from polarization conversion to high absorption. In order to engineer novel materials consisting of self-assembled nanostructures, a comprehensive understanding of the resonant properties of the individual components is necessary.

# 5.2 Optical Properties of Single Nanostructures

In this section, we present the optical properties of self-assembled nanostructures consisting of the noble metals Au and Ag in the visible range of the electromagnetic spectrum. Initially, we present the response of isolated structures ranging from single NPs to collections of up to seven NPs, including their polarization dependence. Next, using a trimer as a model system, we discuss the effect of the surrounding medium on the LSPR. Specifically, the resonant wavelength is redshifted from 530 to 600 nm as the index changes from 1 to 1.6, useful for sensing applications where the color visually changes based on the dielectric environment (i.e., from green to orange). Further, we elucidate the effect of chemical composition on the plasmonic response by replacing the outer valence NPs from Au to Ag. Accordingly, we introduce a second resonant peak in the blue region of the visible spectrum (<500 nm) that originates from the incorporation of Ag in the nanostructure. For rational design of metasurfaces, we suggest the combination of individual trimers into well-defined planar arrangements where we have exquisite control of the wavelength of maximum absorption. Most notably, we obtain dual-band absorption that strongly depends on incident polarization and can be tuned throughout the visible spectrum by changing the relative separation of the individual building blocks (trimers). This section provides a guideline for the development of advanced metamaterials with a well-controlled and dynamic optical response that can be used as an adaptable coating for high absorption, polarization conversion, and light filtering.

First off, we briefly present the size dependence of the plasmon resonance in single NPs, which can be seen in the extinction spectra plotted in Fig. 5.2 for Au spheres with diameters ranging from 50 to 250 nm. As expected, we find that the magnitude of the extinction cross section raises significantly with increasing size. Additionally, as the NP diameter increases beyond 150 nm, we obtain a second peak that corresponds to the quadrupole excitation, whereas the dipole mode redshifts and broadens significantly from 530 to 680 nm. This broadening is due to radiative damping that becomes more significant with larger NPs. On the other hand, the dipole resonance in smaller NPs is shifted to higher energies, and absorption due to interband transitions occurs and competes with the plasmonic resonance. Accordingly, for the remainder of this section, we constrain our attention to NPs of sizes >10 and <50 nm. These sizes exhibit a well-defined, narrow dipolar response that does not suffer from radiative broadening and has a lower resonance



FIG. 5.2 Extinction cross section for Au nanoparticle spheres with diameters going from 50 to 250 nm.



**FIG. 5.3** First row: schematic of the metallic nanostructures from AB to  $AB_6$ . (a–f) Normal incident extinction spectra for *p* (*solid*)- and *s* (*dashed*)-polarized incident light of the supracolloids. Electric field intensity distribution for *p* (g–l)- and *s* (m–r)-polarized light at the extinction peak, projected on the *x*-*y* plane with a total area of  $100 \times 100 \text{ nm}^2$ . In all cases, the nanoparticles are made of Au and capped by a 10 nm-thick dielectric layer, mimicking BCP tethers or ligands fastened on the NP surfaces.

energy than the interband transition; thus, we are assured that our results are primarily a consequence of the plasmonic properties alone.

Shifting our focus on nanostructures containing two or more NPs, we begin by defining six different geometries that are illustrated in Fig. 5.3. All structures contain a central NP (A) and a varying number of outer NPs (B). The diameters of *A* and *B* are  $d_A = 36$  nm and  $d_B = 22$  nm, respectively, with a 5 nm gap between the NPs. Each NP is capped by a 10 nm-thick dielectric layer of index n = 1.5 to mimic the ligands and BCPs that typically coat the surface of colloidal NPs [16,19]. For our simulations, we define *p*-polarized light for AB and AB<sub>2</sub> aligned on the longitudinal axis of the structure and *s*-polarized along the transverse axis. For the other structures, we define the *p*-polarized light points along the symmetrical axis of the nanostructure with *s*-polarized incident light. As expected, our results show a well-defined resonant peak between 550 and 600 nm. Looking at the low-valence structures (AB and AB<sub>2</sub>), there is a significant redshift of the peak from 540 to 575 nm for AB (Fig. 5.3a) and 600 nm for AB<sub>2</sub> (Fig. 5.3b) as we switch from *s*- to *p*-polarized light due to the coupling between NPs of the plasmon oscillations that occurs when the field is

along the longitudinal axis. Further, as shown in Fig. 5.3c and d,  $AB_3$  and  $AB_4$  structures show a polarization-independent extinction spectra, a behavior consistent with what has been previously reported [21]. The independence of incident light polarization is crucial for sensing applications, where we can obtain a strong response under normal light illumination in microscopes.  $AB_5$  provides a higher extinction cross section for *p*-polarized light when compared with *s*-polarized; however, the resonant peak is at the same energy. For  $AB_6$ , the size of the resonant peaks is equal for both polarizations with *p*-polarized being slightly blueshifted (around 10 nm). The modest higher energy of the peak for *p*-polarized originates from coupling between the central NP with only two valence NPs that results from the orientation of the structure on the glass substrate.

Fig. 5.3g–r presents the *x*-*y* plane, near-field intensity distributions at the peak field enhancement wavelengths for p (g–l)- and s (m–r)-polarized light with the direction of the electric field defined by the arrows in (g) and (m). The size of each map is  $100 \times 100 \text{ nm}^2$ . The profiles are obtained by a Fourier transform of the fields from the time to the frequency domain.

Immediately, we notice a high concentration of the fields confined to the regions between the NPs, known as plasmonic "hot spots," which is useful for applications such as surface-enhanced Raman spectroscopy [22] and second or third harmonic generation [23]. Further, we notice a significant difference in the local distribution depending on the light polarization. For AB and AB<sub>2</sub>, *s*-polarized light excites dipole modes perpendicular to the longitudinal axis and leads to no coupling between the NPs and therefore no hot spots. Conversely, if the polarization has any component directed between NPs, an extended, collective plasmon will be excited (see hot spots in Fig. 5.3g–l and o–q).

The properties of the LSPR in metallic nanostructures strongly depend on the refractive index contrast of the metal and the dielectric environment. Accordingly, we calculate in Fig. 5.3a the extinction for *p*-polarized incident light for individual NPs, which shows a redshift from 520 to 560 nm. Fig. 5.4B shows the extinction spectra for an  $AB_2$  trimer as



**FIG. 5.4** Simulated extinction cross section for *p*-polarized incident light of (A) a Au NP with diameter d = 36 nm and (B) a Au trimer with NP diameters d = 22, 36, and 22 nm as the refractive index of the surrounding medium is varied from 1.0 to 1.6. Insets: schematic illustrations of simulated structures.

we vary the index of the surrounding media. Our results show a strong redshift of the LSPR peak from 530 to 600 nm as the refractive index *n* is varied from 1.0 to 1.6. The coupling of the LSPRs between NPs is heavily dependent on the hot spots generated between NPs. Evidently, the intensity of these hot spots increases with higher index, indicating a more pronounced redshift of the plasmon resonance in the trimer compared with the individual NP. The heightened sensitivity of the dielectric environment for this supracolloid makes it a compelling candidate for sensing applications [24–26].

To demonstrate how the optical response of the nanostructures can be further manipulated, we vary the chemical composition of the outer valence nanoparticles. As a reference, Fig. 5.5A shows the extinction spectra for pure Au trimers. Fig. 5.5B shows the extinction spectra for a trimer with the outer NPs consisting of Ag instead of Au. Here, we observe two resonant peaks for both polarizations with the *s*-polarized excitation occurring at higher energy than the *p*-polarized. With the inclusion of the Ag, we gain a resonant peak under 450 nm for both polarizations. Further, we see that the AuAg<sub>2</sub> structure has less redshift of the LSPR peak compared with the pure Au trimer. This is a direct consequence of the fact that the excitation energy in Ag is higher than Au [8], which means that all three NPs cannot get excited and form a collective LSPR. However, the electrons in the Ag NPs form an off-resonance dipole oscillation that interacts with the Au plasmon under *p*-polarized incident light that leads to a small redshift in the cross-sectional scattering. This result is apparent in Fig. 5.5, where the redshift for the *p*-polarized extinction is approximately 20 nm for AuAg<sub>2</sub> compared with 45 nm for pure Au.

#### 5.3 Towards Self-Assembled Metasurfaces

In this section, we discuss the use of collections of colloidal NPs as building blocks for metasurfaces with tailored optical responses. As a proof of concept, we focus on linear



FIG. 5.5 Simulated extinction cross section for a trimer with (A) a central 36 nm Au NP and two outer 22 nm Au NPs and (B) an identical trimer made by substituting the two outer NPs with Ag for p (solid)- and s (dashed)-polarized incident light. Insets: illustrations of the trimers used in the simulations.



**FIG. 5.6** (A) Simulated absorption spectra for *p*-polarized incident light of a metasurface formed from trimers (with 22 and 36 nm Au nanoparticles) in the vertically stretched (chain), relaxed (packed), and horizontally stretched (ribbon) states. (B) Schematic illustration of the different surfaces. (C) Simulated absorption spectra for *s*-polarized incident light.

arrangements of trimers (see Fig. 5.6). Several assembly methods could potentially be used to create such arrays including template-assisted self-assembly or DNA-assisted assembly [13,20,27]. If the surface is deposited on a stretchable substrate, one could obtain a dynamic optical response that depends on the spacing between the individual building blocks [28,29]. In Fig. 5.6, three arrangements are defined as chain, packed, and ribbon structures. The sizes of the NPs are 36 and 22 nm, with a minimum separation distance of 5 nm for every neighboring NP. Fig. 5.6A presents the absorption spectrum for incident light polarized along the longitudinal axis of the trimers. Depending on the relative spacing between the trimers, we have either a redshift or a blueshift of the absorption maximum with respect to the packed state. Moreover, in the packed state, there is a broad range of light absorption spanning about 200 nm. For s-polarized light, there is a drastic shift of the resonance from 520 to 675 nm while switching from a chain arrangement to a ribbon (see Fig. 5.6C). In addition, there is a second peak that emerges in the packed and ribbon state close to 550 nm. This peak is due to a second, collective longitudinal plasmon mode between the smaller NPs that are too isolated from one another in the chain structure to couple effectively. These surfaces allow the control of light polarization in wavelengths >550 nm, where only the *s*-polarized light is absorbed, enabling the dynamic switching of light polarization through perturbing the surface in the in-plane directions.

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To better visualize the behavior of the metasurfaces under optical excitations, Fig. 5.7 explores the near-field distribution of the Au chain discussed above at the absorption peak of ~576 nm. The *x*-component of the electric field ( $E_x$ ) has a strong negative value in the region between the NPs and a positive value within the NPs. This could indicate the importance of the small gap between the NPs in forming the collective long-range plasmon oscillation along the chain. Fig. 5.7B maps the *y*-component of the electric field ( $E_y$ ). Here,  $E_y$  resembles a collection of quadrupoles where we have four corners of opposite signs for each NP. In addition, we see an absence of  $E_y$  along the longitudinal axis of the chain and along the *y*-axis at the center of the larger NPs. Finally, Fig. 5.7C shows the *z*-component ( $E_z$ ), which is directed normal to the plane of the map. Similar to  $E_y$ , there is no  $E_z$  along the center of the larger NPs, and the distribution looks like that of a collection of electric dipoles in series. Overall, it appears that  $E_x$  is the component resulting from the coupling between NPs and  $E_y$  and  $E_z$  demonstrate the multipole behavior of the plasmon oscillations.

For further control of the optical response of arrays consisting of trimers, one can replace the outer valence NPs with Ag, as displayed in Fig. 5.8. For *p*-polarized light (Fig. 5.8A), we observe three resonant peaks in the blue region of the visible spectrum resulting from the Ag NPs compared with surfaces containing only Au NPs that contain only a single peak. The central peak is suppressed in the ribbon state due to the absence of LSPR coupling between the adjacent Ag NPs that is present in both the chain and packed states. Further, the resonant peak at 425 nm remains fixed for all arrangements, whereas the peak at 540 nm (blue) shifts to 575 nm (red) from the ribbon to the chain. Fig. 5.8C shows the absorption spectrum for *s*-polarized light. Here, the surface has two absorption maxima: a high-energy peak at 450 nm and a lower energy peak that can be tuned from 540 to 660 nm.



FIG. 5.7 Top row: schematic of Au chain used in calculations. In-plane electric field distribution for the (A) x-, (B) y-, and (C) z-components at the absorption peak of 576 nm excited by p-polarized incident light. The distribution is implicitly normalized by the modulus of the incident plane wave.



**FIG. 5.8** (A) Simulated absorption spectra for *p*-polarized incident light of a metasurface formed from trimers (with two 22nm Ag and 36nm Au nanoparticles) in the vertically stretched (chain), relaxed (packed), and horizontally stretched (ribbon) states. (B) Illustration of the different surfaces. (C) Simulated absorption spectra for *s*-polarized incident light.

### 5.4 Metal Alloyed Nanoparticles

Nanostructuring alone offers a good way to control the resonant properties of metals. However, as stated earlier in this chapter, alloyed nanostructures formed by metals can enable the tunability of the material's optical response beyond the behavior currently observed for pure metals. Specifically, by alloying metals, we effectively change the dielectric function of the material. An example is presented in Fig. 5.9, where the permittivity ( $\varepsilon_1$  and  $\varepsilon_2$ ) of the pure metals, Au and Ag, and a 50% mixture of the two are plotted as a function of wavelength. The dielectric function of the metals was obtained via ellipsometry, where we use elliptically polarized light and measure both its phase and amplitude shift as it is reflected off the surface of a thin film and the transmission intensity. The results are obtained by modeling the system as a single metal layer above a glass substrate. During the fitting, we use a b-spline model to match the measured phase and amplitude shift, as well as transmission intensity, to obtain the permittivity and film thickness of the sample. After several iterations, the results converge, and the optical constants of the b-spline modeled metal are extracted.

The dielectric functions acquired through ellipsometry allow us to calculate the optical behavior of metal-alloyed nanostructures using simulations. For example, Fig. 5.10 presents the transmission calculated as a function of both the NP size and the composition. For each composition, up to 184 nm in diameter, our calculations predict a slight blueshift



**FIG. 5.9** (A, C, E) Real ( $\varepsilon_1$ ) and (B, D, F) imaginary part ( $\varepsilon_2$ ) of the permittivity obtained via fitting ellipsometry measurements for Ag (left), Ag<sub>0.5</sub>Au<sub>0.5</sub> (middle), and Au (right).



FIG. 5.10 Macroscopic transmission of NPs going from pure Au to pure Ag as the diameter of the NPs is varied from D=53 (left) to 441 nm (right).

in the transmission valley (related to the plasmon resonance) followed by a redshift as the composition is changed from pure Au to pure Ag. Accordingly, we anticipate that the combination of size with composition allows for great control of the plasmonic properties of NPs while implementing fabrication methods that can be scaled up, to be described in greater detail below.

Going a step further, we can also perform calculations, using the alloy permittivity as input, of ordered arrangements of nanostructures that can be fabricated via electronbeam lithography. Fig. 5.11 presents an example of predicting the scattering response of metal oligomers containing either Au, Ag, or Au<sub>0.5</sub>Ag<sub>0.5</sub>. The oligomer is a classic example of Fano resonance that is apparent in the scattering spectrum as the sharp dip due to the energy transfer from the bright radiant mode, where all excited dipoles within the NPs are parallel to each other, to a dark mode. By alloying the metals, we can maintain the



FIG. 5.11 Calculated scattering spectra for Ag, Au<sub>0.5</sub>Ag<sub>0.5</sub>, and Au oligomers. Top right: schematic illustration of oligomer used in the calculation.

same geometry while controlling the spectral position of the Fano resonance. Specifically, we predict a slight blueshift of the resonance of the alloys when compared with the pure metals.

Although numerical calculations can be a powerful tool for predicting the optical behavior of metal and metal-alloyed nanostructures, the actual implementation of nanoscale systems for photonics requires knowledge in advanced fabrication techniques. For the remainder of this section, several relevant fabrication processes will be discussed along with their advantages and limitations. First, a promising route to obtain large-scale areas (wafer size) of alloyed NPs is known as the "thin-film deposition" followed by annealing process. As displayed in Fig. 5.12, the first step consists of depositing the metals of interest using cosputtering. Here, the chemical composition of the film is adjusted by



FIG. 5.12 (A–E) Illustration of lithography-free process for obtaining self-assembled metallic nanoparticles. First, cosputtering is used for the deposition of alloyed thin films (or a single sputtering source is used for obtaining a pure metallic film). The substrate is constantly rotating to assure uniform film composition and thickness. Second, the film is annealed in a controlled environment, and the nanoparticles are formed by dewetting. (F) SEM image of Ag-Au nanostructures with controlled chemical composition obtained by this process.

simply calibrating the deposition rate of each source. The substrate is rotated to assure the uniform deposition of all metals. Second, once a metallic thin film (usually with thickness <20 nm) is fabricated, the sample undergoes an annealing process in a controlled environment of either N<sub>2</sub> or Ar. During this process and depending on the materials involved, substantial surface diffusion occurs at the film/substrate interface to minimize the surface and edge energy terms of the enthalpy, resulting in the formation of nanostructures. Fig. 5.12 shows an example of Ag<sub>0.5</sub>Au<sub>0.5</sub> NPs obtained by this fabrication method. Note that the size and distribution of these NPs primarily depend on (i) the metals involved, (ii) the substrate, (iii) the thickness of the deposited film, (iv) the annealing temperature and time, and (v) the gas flow during the annealing step.

A primary advantage of this process is the fact that it can be easily scaled up: 6 in wafers can be covered with metallic nanostructures using a fairly simple procedure. Further, the NPs can be formed on a dielectric substrate and also capped by another dielectric (such as a polymer), providing an easy pathway for a metal-insulator-metal (MIM) system. Nevertheless, the simplicity of this method is limited by the broad size and shape distribution of the NPs, as observed in Fig. 5.12F.

Alternative methods to acquire arrays of NPs with very uniform size distribution are electron-beam (e-beam) lithography and through template deposition. E-beam lithography is a serial process in which selective areas of a substrate coated with a resist, usually poly(methyl methacrylate), are exposed to a well-focused, scanning electron beam. Upon exposure, the resist decomposes and is later removed by a developing agent, leaving only the unexposed resist. Next, the exposed substrate can be etched to form holes and valleys, or a material can be deposited, and the excess is removed via a liftoff of the remaining resist to form NPs. While exquisite, nanoscale resolution can be obtained using e-beam lithography, the serial nature of the process causes it to be time-consuming and expensive.

To overcome the scalability constraint of e-beam lithography and maintain high spatial control of the NPs, the deposition of the metal(s) can be made through templates (masks). As displayed in Fig. 5.13, a predesigned mask is applied to the desired substrate, and the metal(s) is (are) deposited through. Fig. 5.13D shows a SEM image of an array of Ag-Al NPs attained by using a  $Si_3N_4$  template. To obtain a mixture of metals, two options can be implemented. In the first one, the metals can be deposited simultaneously while rotating the substrate + template stack. This method requires a deposition system with the capability of dual evaporation. For the second approach, the sequential deposition of thin layers of the metals, followed by an ex situ annealing step, promotes intradiffusion of the atoms and the formation of an alloy when allowed by the mixing enthalpy of the elements involved [30].

#### 5.5 Optical Response of Metal-Alloyed Nanoparticles

The near- and far-field optical responses of metal-alloyed nanostructures frequently differ from the properties of their constituents as the LSPR occurs at wavelength that differs



FIG. 5.13 Schematic illustration of (A) metal deposition through a template, (B) removal of the template, and (C) array of metallic nanostructures with well-defined size, shape, and periodicity. (D) SEM image for metallic nanocylinders with a diameter of 500 nm fabricated by this through template deposition method.

from the pure metals. In this final section, we briefly introduce the concept of near-field scanning optical microscopy (NSOM) and use Ag-Au as a model system to explain how local electric field enhancements can be obtained at different wavelengths by alloying these metals.

The process of how NSOM operates is illustrated in Fig. 5.14A. In this schematic, evanescent waves are used to break the far-field diffraction limit [31]. By keeping the distance between the probe and the sample surface considerably smaller than the wavelength of light ( $d \ll \lambda$ ), we can map near-field interactions of the sample at the nanoscale. The probe, 60–200 nm in diameter at the apex, scans the surface of the sample, similar to the needle of a record player, collecting information about the topography of the nanoparticles. Simultaneously, an objective lens collects the light transmitted through the sample (and the



FIG. 5.14 (A) Cross-sectional schematic illustration of near-field scanning optical microscopy (NSOM) performed on an array of metallic nanoparticles on top of an indium tin oxide (ITO)/glass substrate. (B) Topography and (C) NSOM transmission map of Ag<sub>0.5</sub>Au<sub>0.5</sub> nanoparticles upon 600 nm excitation.

glass slide in this case). Thus, NSOM is an ideal imaging tool to quantify and spatially map *where* the LSPR occurs. Fig. 5.14B and C shows the topography and transmission signals of the Ag<sub>0.5</sub>Au<sub>0.5</sub> NPs.

The transmission is acquired upon exciting the nanostructures at their resonance, using a 600 nm laser, and collecting the transmitted light. The high signal occurs underneath and around the edges of the NPs and corresponds to the electric field enhancement caused by the particles' LSPR at this wavelength.

NSOM measurements are often accompanied by full-field simulations of the electric field profile ( $|E|^2$ ), which provide a complete description of the relevant light-matter interactions. As an illustration, Fig. 5.15 displays a schematic of the alloyed NP and the corresponding simulation. Note the very good agreement between the experimental and the computational results presented in Figs. 5.14 and 5.15, respectively. Here, we use a dipole as the excitation source, at 600 nm for direct comparison with the NSOM measurements. The size, geometry, and periodicity of the NPs are obtained from the atomic force microscopy (AFM) scans, as presented in Fig. 5.14B. Because the permittivity of the metal alloys differs substantially from the linear combination of its pure counterparts weighted by chemical composition, we determine this quantity experimentally by combining transmission and reflection measurements of alloyed thin films through ellipsometry (as described above). The value is then incorporated as a realistic input into the full-field simulations.

### 5.6 Summary

In this chapter, we presented the optical properties of colloidal nanoparticles as potential building blocks for metasurfaces. We showed the near- and far-field properties for clusters



**FIG. 5.15** (Left) Cross-sectional schematic of metallic nanoparticle on top of an indium tin oxide (ITO)/glass substrate. (Right) Profile for electric field distribution of  $Ag_{0.5}Au_{0.5}$  with  $253 \pm 62$  nm in diameter and  $126 \pm 40$  nm in height. The color scale refers to the intensity of the modulus square of the electric field. For the simulation, dipole source at 600 nm. Reproduced with permission from C. Gong, M.S. Leite, Noble metal alloys for plasmonics, ACS Photon. 3 (2016) 507–513. Copyright 2016 Wiley-VCH Verlag GmbH & Co KGaA, Weinheim.

of up to seven NPs that revealed strong field enhancement in the regions between the particles depending on the incident electric field. Moreover, we demonstrated a polarizationindependent far-field response for  $AB_3$  and  $AB_4$ , which is useful for sensing applications. In the sequential sections, we focused on the  $AB_2$  trimer and quantified the sensitivity of the optical response to the local dielectric environment and the relative composition of the NPs by replacing the outer Au NP with Ag. We find a second resonant peak in the short-wavelength portion of the visible spectrum resulting from the existence of Ag. Moreover, we presented a dynamic metasurface with single- and dual-band resonant peaks by constructing linear arrangements of AB<sub>2</sub> trimers. The self-assembled nanostructures potentially allow for precise control of light polarization and well-engineered absorption throughout the visible wavelength range. The combination of colloidal nanoparticles with BCPs or DNA tethers will enable programmable self-assembled nanostructures that can be useful for applications such as conformal coatings for perfect absorbers, polarization converters, and sensors. Further, we showed that cosputtering followed by annealing provides an appealing, scalable technique for obtaining fully alloyed nanoparticles with an on-demand optical response. Lastly, in this chapter, we mapped the near-field response of fully alloyed AuAg using NSOM and found excellent agreement with numerical calculations. A 30 times field enhancement on resonance is observed due to the excitation of the LSPR of the NP.

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