We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Plasmonic Field Distribution of Homo- and Hetero Dimeric Ag and Au Nanoparticles

Nasrin Hooshmand

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67411>

Abstract

Silver (Ag) and gold (Au) nanoparticles are known to have very strong plasmonic fields among the other plasmonic metallic nanoparticles. When two Ag or Au nanoparticles are brought close together, hot spots (strong electromagnetic field) are formed between the particles, which can be exploited in imaging and sensing applications. In this chapter, we used the discrete dipole approximation (DDA) to investigate the interdimer separation dependence of the localized surface plasmon resonance (LSPR) of homo- and heterodimers of Ag and Au nanocubes (NCs) when the exciting incident light is polarized parallel to the dimer axis. It was found that as the interdimer separation changes, the plasmonic field distribution around the nanocubes' surface varied. The results from the homodimers showed that the primary plasmon band red-shifted in accordance with the universal scaling law and the hot spots geometry changed abruptly at small separations. The results simulated at very short distances showed that the hot spots formed in between the adjacent facets and away from the corners of these facets. However, at larger separations, it moved toward the adjacent corners. For heterodimers, unusual behavior was observed. It showed that the E-field resulting from excitation of the Ag-dominated plasmon resonance was significantly weaker than expected, and the red shift of the gold-dominated plasmon resonance did not follow the universal scaling law. It is likely that the silver plasmon mixes with the gold interband transition to form a hybrid resonance that produces weaker overall field intensity.

Keywords: plasmonics, DDA, coupling, nanoparticles, dimer

1. Introduction

Plasmonic nanoparticles made of Ag or Au received significant attention from researchers as it showed unique properties when they interact with the electromagnetic radiation, primarily in the visible region. The localized surface plasmon resonance (LSPR) is an example for one such property. This results from the resonant excitations of the collective oscillations of their conduction band electrons [1–4]. The LSPR is tunable and strongly dependent on the shape, size, composition, and relative dielectric function of the nanostructure [4–11]. The oscillation of the electrons results in a strong enhancement in the optical absorption, scattering and near-field intensities of noble metal nanoparticles allowing for their use in numerous applications such as biological imaging, selective photothermal therapy, surface enhanced Raman scattering (SERS), optical wave guiding, and biochemical sensing [12]. It is well known that as interparticle gaps are reduced, localized regions of intense electromagnetic fields known as “hot spots” [13, 14] will be formed, which are of interest in surface-enhanced Raman spectroscopy (SERS). This is primarily due to the spatial overlap of the individual plasmonic modes, which induces the formation of hybridized collective plasmonic modes. At nanoscale separations, the hot spots produced in these composite frameworks exhibit noteworthy enhancements in Raman scattering, fluorescence, infrared absorption; which has been useful for a variety of applications [15–17]. Substantial Raman enhancement can be generated, using larger aggregates experimentally [18].

The effect of coupling between the surface plasmons of adjacent particles, such as in nanoparticle aggregates, is very important and has received a great deal of attention in recent years. Coupling typically results in a shift in the LSPR wavelength and a great enhancement of the plasmonic electromagnetic field (E-field) [19, 20]. This is important in optical technologies such as chemical and biological imaging [21, 22], sensing [23–25], and therapeutics [26–29]. This interparticle plasmon coupling forms the basis of the intense enhancement of spectroscopic signals (e.g., SERS) from molecules adsorbed at nanoparticle junctions, providing the capability for single-molecule sensing and detection [30, 31]. The overall strength of coupling depends on the polarization direction of the exciting field and the distance between the nanoparticles. It has been observed that the LSPR shift due to coupling decreases exponentially with increasing interparticle distance [20, 32]. When normalized to particle size, the relationship holds for many nanoparticles with different sizes, shapes, metals, and media; this has been termed the universal scaling law [19, 33].

Ag and Au NCs with sharp corners are known to have very strong plasmonic fields concentrated at their corners. The study of the coupling between a pair of Ag NCs and the effect of rounding the cube corners on their coupling strength has recently been carried out [34]. This chapter will focus on the theoretical understanding of unique features of assembled nanocubes made of Au and/or Ag plasmonic nanoparticles in face-to-face (FF) orientation. Discrete dipole approximation (DDA) method has been used to study the distance dependence of the plasmonic field coupling between homodimers (Ag-Ag or Au-Au) and heterodimers (Ag-Au) of nanocubes with sharp corners. We examined the dependence of the interaction of particles with light at the interparticle separation gap. Finally, we looked at the LSPR extinction wavelength and the relative field intensity distribution and the hot spot formation (strong E-Field) between adjacent nanoparticles at small interparticle separations.

2. Research methods

Modeling and simulation play a key role in the advancement of nanoscience and nanotechnology. Among various numerical methods, DDA received significant attention as it can provide useful information on plasmonic phenomena. The DDA [35] is one of the most powerful theoretical techniques to model the optical properties of plasmonic nanoparticles of arbitrary geometry. This method was used to calculate near field interaction between of closely placed cubic Ag and Au nanoparticles (edge length = 42 nm) assembled in face-to-face orientation. The refractive index of Ag and Au NCs is assumed to be the same as that of the bulk metal [34]. The surrounding medium was set to be the water ($n = 1.33$). Simply, in DDA, the target (here Ag and/or Au NCs) represents as cubic arrays of several thousands of points acquire dipole moment in response to the local electric field located on a cubic lattice (with volume d^3). Details of the DDA method have been described elsewhere [35–37]. One of the important prospects of the LSPR to understand is the effect of the electromagnetic field distribution in determining sensing performance of the metal nanoparticles. This needs to go through the fundamental study of the plasmonic properties of nanoparticles. Using DDA [35, 37], we were able to calculate the plasmonic properties such as plasmonic field distribution of a pair of homo- and heterodimeric nanocubes made of Au and Ag at different separations upon exposure to resonant incident electromagnetic field. The Plasmonic field enhancement factor (in log-scale of $|E|^2/|E_0|^2$) was located on the surface of a dimer of cubes with the DDA technique at different excitation wavelengths.

3. Gold nanocube dimer

Plasmonic nanoparticles dimers are very important in this context due to large electromagnetic field formation between them when they are in close proximity and exposed to the incident light [32, 38–41]. The strong electromagnetic field (hot spot) only forms, if the incident light polarized along the dimer axis [42]. **Figure 1a** and **c** shows, as the separation distance between the cubes decreases, the intensity of the SPR bands enhances and red-shifts. The total extinction increases from 5 a.u. for a single particle (or a large separation) to 18 a.u. for 2 nm separation. The extinction band maximum red shifts from 588 to 642 nm, upon decreasing the separation gap between the cubes. These results follow the typical scaling law seen for other particles (**Figure 1b**).

To better understand the dipole coupling behavior between the two nanocubes, the E-field plasmonic enhancement was calculated for a single and the dimer of Au NCs at very short distance (2 nm) and larger distance (10 nm). For calculating the field distribution of single and dimer of Au NCs, the maximum plasmon band wavelength of interest was used to excite the single or dimeric nanoparticles. We excited the single Au NC at 585 nm, a dimer with 2 nm of separation at 641 nm, and a dimer with 10 nm separation at 613 nm (**Figure 2a–c**).

The E-field around the single nanocube showed the characteristic pattern of field concentrated at the corners. As the particles moved away (at 10 nm), it shows that the electromagnetic field became stronger near the adjacent corners compared to the adjacent facets. When the separation is reduced to 2 nm, the E-field strength moved away from the adjacent corners and in between the facing facets of the dimer.

Figure 1. (a) Dependence of the extinction spectra on the separation distance of an Au NCs dimer in water. (b) Exponential behavior of fractional plasmon shift ($\Delta\lambda/\lambda_0$) as a function of the interparticle separation normalized by the length of the nanoparticle. (c) The exponential dependence of extinction maximum on the interparticle separation. This exponential dependence suggests that the extinction spectra of Au NC dimers follow the universal scaling law. Reprinted with permission from Ref. [41]. Copyright 2014 American Chemical Society.

Figure 2. Plasmonic field enhancement for (a) single Au cube, (b and c) the dimer of Au-Au NCs with 2 nm of separation (excited at 641 nm) and 10 nm of separation (excited at 613 nm). As the separation distance increases to 10 nm, each cube in the dimer likely has the E-field distribution in character like which shown for the single cube. However, at 2 nm, the strongest field is located at the center of the adjacent faces. Reprinted with permission from Ref. [41]. Copyright 2014 American Chemical Society.

4. Silver nanocube dimer

In order to compare our results with a pair of Au NCs, we calculated extinction and field distribution for pairs of Ag NCs in the same condition. The extinction spectra for different separations of homodimer of Ag NCs are shown in **Figure 3a** and **c**.

Figure 3. (a) DDA calculated extinction spectra at different distances, (b) exponential behavior of fractional plasmon shift ($\Delta\lambda/\lambda_0$) as a function of the interparticle separation normalized by the length of the nanoparticle and (c) the exponential decrease of the intensity of the strongest extinction peak as the interparticle separation increases. Reprinted with permission from Ref. [41]. Copyright 2014 American Chemical Society.

It shows that the extinction spectrum of a widely separated pair of cubes is nearly identical to that of the monomer. Contrary to the Au, it was found in the single and dimer Ag nanoparticles that there are two strong bands at long wavelengths (probably dipolar) and two weak higher order polar bands at short wavelengths. As the gap between the cubes decreases, although the bands shift to longer wavelengths, the shorter wavelength bands show further red shift than the longer wavelength bands. While a strong doublet is observed for 60 nm of separation, for 20 nm separation, one band of the doublet becomes weaker and broader in the spectrum. It is possible that the higher order bands become stronger and the higher energy dipolar band is likely to be submerged under the strong higher order band.

As shown in **Figure 3b** with increasing the interparticle gap separation of the Ag NCs dimer, the magnitude of the red shift of the plasmon band decreases based on the universal scaling law [41]. **Figure 4a–c** shows the electromagnetic field distribution of the Ag NCs dimer and single Ag NC. Here, only the main plasmonic band for both single Ag NC ($\lambda_{\text{max}} = 481$ nm) and Ag NCs dimer at 2 nm ($\lambda_{\text{max}} = 553$ nm) and 10 nm ($\lambda_{\text{max}} = 517$ nm) was excited. As the separation distance increases, the E-field distribution becomes similar to the single Au NC.

In order to examine the hybridized dimer modes of the dimer of Ag nanocubes, the electromagnetic field was calculated at 2 and 10 nm separation distances. The results showed that at 10 nm of separation, the field strength is strongest at the corners (**Figure 4c**), whereas, at 2 nm separation, the strongest field moved toward the center of the adjacent faces (**Figure 4b**). Compared to the dimer of the Au NCs, in all cases, the electromagnetic fields for the Ag NCs were stronger, as expected.

Figure 4. (a) Plasmonic electromagnetic field enhancement for a single Ag NC and the dimers of Ag-Ag NCs with (b) a separation distance of 2 nm (excited at 522 nm) and (c) separation distance of 10 nm (excited at 517 nm). As the separation distance decreases, the hot spots formation takes place in between the faces facing of the dimer and away from their corners. However, when the cubes move away from one another, the field distributions are mostly present around the corners of the faces facing facets of the dimer. Reprinted with permission from Ref. [41]. Copyright 2014 American Chemical Society.

5. Plasmon coupling of gold-silver heterodimeric nanocubes

The results for the Ag-Au heterodimeric NCs showed unusual results and more exciting conclusions. We expect that the plasmonic modes of gold and silver will mix to form hybrid modes. Simply, if we consider Ψ_{Au} and Ψ_{Ag} as dipolar modes for gold and silver, respectively, we might think that the two hybrid modes would be $(\Psi_{\text{Au}} + \Psi_{\text{Ag}})$ and $(\Psi_{\text{Au}} - \Psi_{\text{Ag}})$ [41]. However, the hybrid modes will not have equal contribution of Ag and Au uncoupled modes because the energies of the uncoupled modes are so different (gold at 588 nm and silver at 482 nm). As discussed by Sheikholeslami et al. in their work on Au-Ag nanosphere heterodimers [43], because the inter-band transition of gold strongly overlaps energetically with the Ag NC's natural LSPR resonance, the LSPR resonance of the Ag NC may strongly couple to it. We showed at large dimer separations, the spectrum somewhat identical to the summation of the spectra for a single Au NC and an Ag NC, and there is no coupling between the Au and Ag cubes [41]. At short separating distance, mixing occurs between the heterodimer of Au and Ag cubes. The main band around 600 nm showed that significant enhancement in characteristic intensity corresponds to the Au-like plasmonic band. This band red shifts with decreasing separation and showed that the band does not follow the universal scaling law as we showed in the homodimer cubes.

In order to understand the interplay between the Au and Ag NCs, the E-fields were calculated at 2 and 10 nm with different excitation wavelengths. The field resulting from excitation of plasmon band at 2 nm (615 nm) and 10 nm (597 nm) is shown in **Figure 5a** and **b**. It shows that, at 10 nm of separation, the field is largely concentrated around the corners of the gold cube (on the right). In Ag NC dimer, at 2 nm of separation, the E-field enhances due to increased mixing-in of Ag dipolar mode. However, it is still weaker than the field around the Au NC. This hybrid mode can be represented as $\Psi_1 = a\Psi_{\text{Au}} + b\Psi_{\text{Ag}}$ where $a > b$. Just as with the homodimers, the E-field is strongest at the corners and between the facing facets (**Figure 6**).

It shows the field distributing of the heterodimer of Ag-Au nanocubes when exciting the dimer at 487 nm associates with 2 and 10 nm of separations, whereas the hybrid modes have

Figure 5. (a and d) Separating the cubes by 10 nm and exciting at 597 nm produces a field almost entirely located on the Au NC. However, exciting at 487 nm exhibited the same pattern as seen for separation distance of 2 nm. Reprinted with permission from Ref. [41]. Copyright 2014 American Chemical Society. (b and c) Plasmonic electromagnetic field enhancement for the dimers of Ag-Au when the particles are separated by 2 nm (exciting at 487 and 615 nm). It shows that the field is strongest around the corners of the silver cube at 487 nm and exciting at 615 nm, the most field strongest in the middle of facing facets as well as around the exterior corners of the gold cube.

Figure 6. The spectrum of plasmonic coupling model for the heterodimer of Au-Ag NCs separated by 2 nm (left). It shows that there is significant mixing of the plasmonic modes of the two particles to form hybrid resonances at 2 nm. The two strongest bands at 615 and 487 nm associated with the corresponding field distribution in Figure 5b and c. A schematic represents that which modes mix to form the two strongest hybrid modes (right). Au interband transition can mix with Ag dipolar plasmonic resonance (around 487 nm), due to the similarity in energy. Adapted with permission from Ref. [41]. Copyright 2014 American Chemical Society.

more silver character. Herein, for both separations, we can see that the field concentrates around the Ag cubes' corners, and there is no field around the Au cube (**Figure 5c** and **d**). This suggests that this hybrid mode contains little gold dipole character. Compare to what was seen with all other dimeric pairs, as the intercube distance is reduced from 10 to 2 nm, the maximum field enhancement is reduced. This is expected due to the fact that silver's dipole mode hybridizes with gold's interband transition. Exciting the nanoparticle at the interband transition produces an incoherent excitation and little net E-field. Subsequently, a hybrid mode containing significant interband transition-character will produce a weaker overall E-field. We would also expect that there would be little to no E-field located on the Au NC, which was obvious. It is expected that this mode has the form $\Psi_2 = a\Psi_{\text{Au}} + b\Psi_{\text{Ag}} + c\Psi_{\text{IB}}$, where Ψ_{IB} is the interband transition mode and $b > c$ and $a \approx 0$. A schematic overview of the proposed mixing scheme for Au and Ag NCs is shown in **Figure 6** (on the right). The spectrum shows other modes that these high-energy resonances are likely included mostly of silver's higher order modes.

It concludes when exciting the heterodimer at gold plasmon wavelength, reducing the separation distance weakens the field due to the silver plasmon mode mixes with gold's interband transition, and since the interband transition does not show plasmonic behavior, it causes reduction in the overall field enhancement. As shown in **Figure 6** (on the left), the main band (the hybrid band) contains both Au and Ag components, and it is mostly gold-based resonance around 600 nm in character [41].

6. Conclusions

In this chapter, we summarize numerically the dependence of interparticle on the LSPR band shift and electromagnetic field distribution around face-to-face oriented Ag and/or Au NC homo- and heterodimers. To begin to study the plasmonic coupling behavior between cubes, the extinction spectrum was calculated for different separation distances. It was found that the separation distance between the cubes plays a significant role in the plasmonic shift in the extinction spectrum and corresponding E-field around the particles. Exciting homodimers of Au and Ag NCs parallel to the interparticle axis showed results consistent with expectations and follow the typical scaling law seen for other particles. This study is pointing toward the fact that in homodimers NC at very short separation of distance (i.e., 2 nm), the maximum field moved away from the corners of the cubes and became strong between the adjacent faces. Compared to homodimers, different behaviors are observed for the heterodimers. As the Au and Ag cubes in close proximity to each other, their plasmon modes mixed to form hybrid modes. As a result, Au dipolar mode weakly mixed with Ag higher energy dipolar mode. As a result, this hybrid mode enhanced the E-field primarily around the Au NC. Silver's plasmonic mode mixed with gold's interband transition, due to their similar energies. It was found that since the interband transition is an incoherent excitation, it results no E-field, and this hybrid mode had a weaker field enhancement compare to that of un-hybridized Ag mode.

Acknowledgements

The author would like to acknowledge the Georgia Institute of Technology for providing high performance computing resources and support. The author thanks B.T. Draine and P.J. Flatau for use of their DDA Cod DDSCAT 6.1. The financial support of NSF-DMR grant (1206637) is greatly appreciated.

Author details

Nasrin Hooshmand

Address all correspondence to: nhooshmand3@gatech.edu

Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States

References

- [1] Willets KA, Van Duyne RP. Localized surface plasmon resonance spectroscopy and sensing. *Annual Review of Physical Chemistry*. 2007;**58**:267-297
- [2] Hao E, Schatz GC. Electromagnetic fields around silver nanoparticles and dimers. *The Journal of Chemical Physics*. 2004;**120**(1):357-366
- [3] Byers CP, Zhang H, Swearer DF, Yorulmaz M, Hoener BS, Huang D, et al. From tunable core-shell nanoparticles to plasmonic drawbridges: Active control of nanoparticle optical properties. *Science Advances*. 2015;**1**(11)
- [4] Link S, El-Sayed MA. Spectral properties and relaxation dynamics of surface plasmon electronic oscillations in gold and silver nanodots and nanorods. *The Journal of Physical Chemistry B*. 1999;**103**(40):8410-8426
- [5] Anker JN, Hall WP, Lyandres O, Shah NC, Zhao J, Van Duyne RP. Biosensing with plasmonic nanosensors. *Nature Materials*. 2008;**7**(6):442-453
- [6] El-Sayed MA. Some interesting properties of metals confined in time and nanometer space of different shapes. *Accounts of Chemical Research*. 2001;**34**(4):257-264
- [7] Kelly KL, Coronado E, Zhao LL, Schatz GC. The optical properties of metal nanoparticles: The influence of size, shape, and dielectric environment. *The Journal of Physical Chemistry B*. 2002;**107**(3):668-677
- [8] Knight MW, Wu YP, Lassiter JB, Nordlander P, Halas NJ. Substrates matter: Influence of an adjacent dielectric on an individual plasmonic nanoparticle. *Nano Letters*. 2009;**9**(5):2188-2192

- [9] Murray WA, Auguie B, Barnes WL. Sensitivity of localized surface plasmon resonances to bulk and local changes in the optical environment. *The Journal of Physical Chemistry C*. 2009;**113**(13):5120-5125
- [10] Sherry LJ, Chang S-H, Schatz GC, Van Duyne RP, Wiley BJ, Xia Y. Localized surface plasmon resonance spectroscopy of single silver nanocubes. *Nano Letters*. 2005;**5**(10):2034-2038
- [11] Xu G, Chen Y, Tazawa M, Jin P. Surface plasmon resonance of silver nanoparticles on vanadium dioxide. *The Journal of Physical Chemistry B*. 2006;**110**(5):2051-2056
- [12] Maier SA, Atwater HA. Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures. *Journal of Applied Physics*. 2005;**98**(1)
- [13] Bordley JA, Hooshmand N, El-Sayed MA. The coupling between gold or silver nanocubes in their homo-dimers: A new coupling mechanism at short separation distances. *Nano Letters*. 2015;**15**(5):3391-3397
- [14] Hooshmand N, Bordley JA, El-Sayed MA. Are hot spots between two plasmonic nanocubes of silver or gold formed between adjacent corners or adjacent facets? A DDA examination. *The Journal of Physical Chemistry Letters*. 2014;**5**(13):2229-2234
- [15] Campion A, Kambhampati P. Surface-enhanced Raman scattering. *Chemical Society Reviews*. 1998;**27**(4):241-250
- [16] Li Z, Shegai T, Haran G, Xu H. Multiple-particle nanoantennas for enormous enhancement and polarization control of light emission. *ACS Nano*. 2009;**3**(3):637-642
- [17] Fraire JC, Pérez LA, Coronado EA. Cluster size effects in the surface-enhanced Raman scattering response of Ag and Au nanoparticle aggregates: Experimental and theoretical insight. *The Journal of Physical Chemistry C*. 2013;**117**(44):23090-23107
- [18] Osawa M. Dynamic processes in electrochemical reactions studied by surface-enhanced infrared absorption spectroscopy (SEIRAS). *Bulletin of the Chemical Society of Japan*. 1997;**70**(12):2861-2880
- [19] Jain PK, Huang W, El-Sayed MA. On the universal scaling behavior of the distance decay of plasmon coupling in metal nanoparticle pairs: A plasmon ruler equation. *Nano Letters*. 2007;**7**(7):2080-2088
- [20] Rechberger W, Hohenau A, Leitner A, Krenn JR, Lamprecht B, Aussenegg FR. Optical properties of two interacting gold nanoparticles. *Optics Communications*. 2003;**220**(1-3):137-141
- [21] El-Sayed IH, Huang X, El-Sayed MA. Surface plasmon resonance scattering and absorption of anti-EGFR antibody conjugated gold nanoparticles in cancer diagnostics: Applications in oral cancer. *Nano Letters*. 2005;**5**(5):829-834
- [22] Sokolov K, Follen M, Aaron J, Pavlova I, Malpica A, Lotan R, et al. Real-time vital optical imaging of precancer using anti-epidermal growth factor receptor antibodies conjugated to gold nanoparticles. *Cancer Research*. 2003;**63**(9):1999-2004

- [23] Alivisatos P. The use of nanocrystals in biological detection. *Nature Biotechnology*. 2004;**22**(1):47-52
- [24] Haes AJ, Hall WP, Chang L, Klein WL, Van Duyne RP. A localized surface plasmon resonance biosensor: First steps toward an assay for Alzheimer's disease. *Nano Letters*. 2004;**4**(6):1029-1034
- [25] Rosi NL, Mirkin CA. Nanostructures in biodiagnostics. *Chemical Reviews*. 2005;**105**(4):1547-1562
- [26] Hirsch LR, Stafford RJ, Bankson JA, Sershen SR, Rivera B, Price RE, et al. Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance. *Proceedings of the National Academy of Sciences of the United States of America*. 2003;**100**(23):13549-13554
- [27] Huang X, El-Sayed IH, Qian W, El-Sayed MA. Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods. *Journal of the American Chemical Society*. 2006;**128**(6):2115-2120
- [28] Huang X, Jain PK, El-Sayed IH, El-Sayed MA. Determination of the minimum temperature required for selective photothermal destruction of cancer cells with the use of immunotargeted gold nanoparticles. *Photochemistry and Photobiology*. 2006;**82**(2):412-417
- [29] Jain PK, El-Sayed IH, El-Sayed MA. Au nanoparticles target cancer. *Nano Today*. 2007;**2**(1):18-29
- [30] Michaels AM, Jiang, Brus L. Ag nanocrystal junctions as the site for surface-enhanced raman scattering of single rhodamine 6G molecules. *The Journal of Physical Chemistry B*. 2000;**104**(50):11965-11971
- [31] Nie S, Emory SR. Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. *Science*. 1997;**275**(5303):1102-1106
- [32] Su KH, Wei QH, Zhang X, Mock JJ, Smith DR, Schultz S. Interparticle coupling effects on plasmon resonances of nanogold particles. *Nano Letters*. 2003;**3**(8):1087-1090
- [33] Reinhard BM, Siu M, Agarwal H, Alivisatos AP, Liphardt J. Calibration of dynamic molecular rulers based on plasmon coupling between gold nanoparticles. *Nano Letters*. 2005;**5**(11):2246-2252
- [34] Grillet N, Manchon D, Bertorelle F, Bonnet C, Broyer M, Cottancin E, et al. Plasmon coupling in silver nanocube dimers: Resonance splitting induced by edge rounding. *ACS Nano*. 2011;**5**(12):9450-9462
- [35] Draine BT, Flatau PJ. Discrete-dipole approximation for scattering calculations. *Journal of the Optical Society of America*. 1994;**11**(4):1491-1499
- [36] Yang WH, Schatz GC, Van Duyne RP. Discrete dipole approximation for calculating extinction and Raman intensities for small particles with arbitrary shapes. *The Journal of Chemical Physics*. 1995;**103**(3):869-875

- [37] Jensen TR, Schatz GC, Van Duyne RP. Nanosphere lithography: Surface plasmon resonance spectrum of a periodic array of silver nanoparticles by ultraviolet-visible extinction spectroscopy and electrodynamic modeling. *The Journal of Physical Chemistry B*. 1999;**103**(13):2394-2401
- [38] Nordlander P, Oubre C, Prodan E, Li K, Stockman MI. Plasmon hybridization in nanoparticle dimers. *Nano Letters*. 2004;**4**(5):899-903
- [39] Atay T, Song J-H, Nurmikko AV. Strongly interacting plasmon nanoparticle pairs: From dipole-dipole interaction to conductively coupled regime. *Nano Letters*. 2004;**4**(9):1627-1631
- [40] Marhaba S, Bachelier G, Bonnet C, Broyer M, Cottancin E, Grillet N, et al. Surface plasmon resonance of single gold nanodimers near the conductive contact limit. *The Journal of Physical Chemistry C*. 2009;**113**(11):4349-4356
- [41] Hooshmand N, O'Neil D, Asiri AM, El-Sayed M. Spectroscopy of homo- and heterodimers of silver and gold nanocubes as a function of separation: A DDA simulation. *The Journal of Physical Chemistry A*. 2014;**118**(37):8338-8344
- [42] Li G-C, Zhang Y-L, Lei DY. Hybrid plasmonic gap modes in metal film-coupled dimers and their physical origins revealed by polarization resolved dark field spectroscopy. *Nanoscale*. 2016;**8**(13):7119-7126
- [43] Sheikholeslami S, Jun Y-w, Jain PK, Alivisatos AP. Coupling of optical resonances in a compositionally asymmetric plasmonic nanoparticle dimer. *Nano Letters*. 2010;**10**(7):2655-2660

IntechOpen