Metallic nanoparticle's localized surface plasmon resonance effect and its application in transparent projection display

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**Metallic nanoparticle's localized surface plasmon
resonance effect and its application in transparent
projection display**

Ye Yiyang

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2019

**Metallic nanoparticle's localized surface plasmon
resonance effect and its application in transparent
projection display**

Ye Yiyang

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

27/06/2019

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Date

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A/Prof Chen Tupei

Authorship Attribution Statement

This thesis contains material from 5 papers published in or submitted to the following peer-reviewed journals where I was the first author.

Chapter 2 is partially adapted from the published paper: Ye Y Y, Liu Z, Chen T P, " Toward transparent projection display: recent progress in frequency - selective scattering of RGB light based on metallic nanoparticle's localized surface plasmon resonance," Opto -Electron Adv 2, 190020, 2019.

The contributions of the co-authors are as follows:

- I did the literature review and wrote the manuscript.
- Prof Zhen Liu helped to review and revise the manuscript.
- A/Prof Tupei Chen guided me on this study and revised the manuscript.

Chapter 4 is published as Y. Ye, T. Chen, J. Zhen, C. Xu, J. Zhang, and H. Li, "Resonant scattering of green light enabled by Ag@TiO₂ and its application in a green light projection screen," Nanoscale, vol. 10, pp. 2438-2446, 2018. DOI: 10.1039/C7NR07383F.

The contributions of the co-authors are as follows:

- I conducted the experiments and simulations and wrote the manuscript.
- A/Prof Tupei Chen guided me on this study and revised the manuscript.
- Mr. Juyuan Zhen inspired me of the original idea and contributed partially to experimental fabrication of transparent film with doctor

blade.

- Dr. Chen Xu discussed with me about the possibility of chemically synthesizing the nanostructure that I proposed and contributed partially to sample fabrication.
- Dr. Jun Zhang contributed partially to UV-visible spectrophotometer measurement and conducted the TEM experiments.
- Dr. Huakai Li contributed partially to simulations and provided some positive suggestions.

Chapter 5 is published as Y. Ye, T. P. Chen, Z. Liu, and X. Yuan, "Effect of Surface Scattering of Electrons on Ratios of Optical Absorption and Scattering to Extinction of Gold Nanoshell," *Nanoscale research letters*, vol. 13, pp. 299-299, 2018. DOI: 10.1186/s11671-018-2670-7.

The contributions of the co-authors are as follows:

- I conducted the simulation as well as the experiments and wrote the manuscript.
- A/Prof Tupei Chen guided me on this study and revised the manuscript.
- Prof Zhen Liu contributed partially to simulation details.
- Mr. Xu Yuan conducted the TEM experiment.

Chapter 6 is published as Y. Ye, R. Liu, Z. Song, Z. Liu, and T. P. Chen, "Sharp selective scattering of red, green, and blue light achieved via gain material's loss compensation," *Optics Express*, vol. 27, pp. 9189-9204, 2019/03/18 2019. DOI: 10.1364/OE.27.009189

The contributions of the co-authors are as follows:

- I conducted the simulations and wrote the manuscript.
- Dr. Rongyue Liu discussed with me about the possibility of

industrializing the proposed nanostructure and contributed to writing of manuscript's introduction.

- Prof Zhen Liu contributed partially to simulation details.
- Dr. Zhigang Song explained to me the physics behind gain material and contributed to explanation of simulated results.
- A/Prof Tupei Chen guided me on this study and revised the manuscript.

Chapter 7 is published as Y. Ye and T. P. Chen, "Selective Scattering of Blue and Red Light Based on Silver and Gold Nanocubes," ECS Journal of Solid State Science and Technology, vol. 8, pp. R51-R57, January 1, 2019. DOI: 10.1149/2.0131903jss

The contributions of the co-authors are as follows:

- I conducted the simulations and wrote the manuscript.
- A/Prof Tupei Chen guided me on this study and revised the manuscript.

27 May 2019
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Date

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Table of Contents

Statement of Originality	I
Supervisor Declaration Statement	II
Authorship Attribution Statement	III
Acknowledgements	VI
Table of Contents	VII
Summary	IX
List of Figures.....	XI
List of Tables	XX
Nomenclatures.....	XXI
Chapter 1. Introduction	1
1.1 Background and Motivation.....	1
1.2 Objective and Scope of research.....	3
1.3 Major Contributions of the thesis.....	4
1.4 Organization of the thesis.....	5
Chapter 2. Literature review.....	7
2.1 General properties of LSPR.....	8
A. Effect of metallic nanoparticle's dielectric function.....	8
B. Effect of metallic nanoparticle's size	12
C. Effect of refractive index of surrounding medium.....	14
D. Effect of particle's shape	15
E. Effect of coating shell.....	17
2.2 Applications of metallic nanoparticle's LSPR	19
A. Selective scattering by spherical core-shell nanoparticle Silica@Ag (core@shell)	21
B. Selective scattering by Ag ellipsoids.....	25
C. Selective scattering by Ag Nanocubes	30
Chapter 3. Methodology.....	35
3.1 Methods for simulating nanoparticle's light scattering and absorption	35
3.1.1 The Mie theory	37
3.1.2 Finite Difference Time Domain (FDTD)	45
3.2 Method to measure material's refractive index	49
Chapter 4. Frequency-selective scattering by core-shell structure of Ag@TiO ₂	52
4.1 Introduction	52
4.2 Theoretical design for green light scattering.....	53
4.2.1 Reasons to choose Ag and TiO ₂ to form the core-shell structure.....	53
4.2.2 Optimization consideration.....	56
4.3 Experimental verification for green light scattering	59
4.4 Theoretical design for red light scattering	65
4.5 Method	66

4.6 Conclusion	72
Chapter 5. Effect of Surface Scattering of Electrons on Ratios of Optical Absorption and Scattering to Extinction of Gold Nanoshell.....	73
5.1 Introduction	73
5.2 Results and Discussion	75
5.3 Methods/Experimental	84
5.4 Conclusion	90
Chapter 6. Sharp frequency-selective scattering of red, green, and blue light achieved via gain material's loss compensation	92
6.1 Introduction	92
6.2 Simulation method	93
6.3 Results and discussion	99
6.4 Conclusion	111
Chapter 7. Frequency-selective Scattering of Blue and Red Light Based on Silver and Gold Nanocubes.....	112
7.1 Introduction	112
7.2 Simulation details	113
7.3 Results and Discussion	114
7.4 Conclusion	131
Chapter 8. Conclusion and Recommendations.....	132
8.1 Conclusion	132
8.2 Recommendations.....	134
List of Publications	136
Bibliography	138
Appendix A	147

Summary

Frequency-selective scattering of light can be achieved by metallic nanoparticle's Localized Surface Plasmon Resonance (LSPR). And this property may find application in transparent projection display: ideally, specially designed metallic nanoparticles dispersed in a transparent matrix only selectively scatter red, green and blue light and transmit the visible light of other colors.

In this thesis, general properties of metallic nanoparticle's LSPR, existing solutions for frequency-selective scattering of light based on LSPR and numerical simulation methods are first reviewed in Chapter 2 and Chapter 3. And the studies reviewed in these two chapters indicate that engineering a metallic nanoparticle's LSPR peak and thus frequency-selective light scattering properties is possible.

Frequency-selective scattering achieved by spherical core-shell structure of Ag@TiO₂ (core@shell) is proposed in Chapter 4. In this chapter, it is shown that frequency-selective scattering of green light can be experimentally achieved by Ag@TiO₂.

Since metallic nanoparticle's size is comparable to free electrons' mean free path in the corresponding constituent metal's bulk form, size effect of metallic nanoparticle on optical scattering and absorption is investigated in Chapter 5. And this effect is shown to broaden light scattering peak width (and therefore decrease frequency-selectivity of light scattering), decrease light scattering strength and increase light absorption strength. Therefore, this effect undesirably degenerates metallic nanoparticle's performance of light scattering in a transparent projection display.

The possibility to achieve ultra-sharp scattering peaks (i.e., strong frequency-selectivity of light scattering) by combining metallic nanoparticles with gain materials is discussed in Chapter 6. Three structures, Silica@Au, Silica@Ag and Ag@Silica, whose Silica are doped with gain material, are proposed. It is shown that these structures generate

sharp frequency-selective light scattering peaks around red, green and blue light, respectively, with low level of light absorption.

Selective scattering properties of silver and gold nanocubes placed on dielectric substrate (TiO_2 or glass) are studied in Chapter 7. Three designs for selective scattering of blue and red light are proposed, of which, only one is found suitable for simultaneous forward and backward selective scattering of blue and red light, the other two are only suitable for either forward or backward selective scattering of blue and red light.

List of Figures

Figure 1.1 Schematic illustration of the concept of transparent projection display achieved by selective scattering of red, green and blue light. This demonstrates the ideal case: light scattering spectrums have ultra-sharp peaks around wavelengths of the three primary colours (red, green and blue), while light absorption remains 0 all through the visible light wavelength range. Figure is taken from reference. ¹⁸	2
Figure 2.1 Electron cloud oscillation, showing the relative displacement of electrons to the nuclei induced by illuminating electromagnetic field. Figure is taken from reference. ¹⁷ ..	8
Figure 2.2 Assuming quasi-static approximation, the sphere feels a spatially constant phase of incident electromagnetic field, as compared to the general case. Figure is adapted from reference. ¹⁶	9
Figure 2.3 Computed extinction cross section spectra with the Mie theory of spherical particles with diameter of 10 nm. (a) Al; (b) Na; (c)Ag; (d)Au, and their corresponding dielectric functions (a') for Al, (b') for Na, (c') for Ag and (d') for Au. Optical constants are from references. ³²	11
Figure 2.4 Extinction spectrums calculated with the Mie theory for spheres of (a) Al, (b) Na, (c) Ag and (d) Au. In figure legends, 2R stands for diameter of a nanosphere. Optical constants are taken from reference. ³²	13
Figure 2.5 Extinction spectrum calculated by Mie's theory for (a) Na in vacuum (refractive index of medium $n=1$), and (b) Na in water (refractive index of medium $n=1.33$). In figure legends, 2R stands for diameter of a nanosphere. Optical constants of Na are from reference. ³²	14
Figure 2.6 (a) The extinction spectrum measured for gold nanorods, taken from reference, ⁴² inset shows TEM image of the gold nanorods, (b) Efficiencies spectrum for an equilateral triangular nanoplate with 100 nm in side length, and 16 nm in thickness, calculated by discrete dipole approximation (DDA), taken from reference. ⁴¹	16
Figure 2.7 Measured extinction spectrums of silver shelled gold (a), with core diameter of 12 nm, and various thicknesses of 0, 0.5, 0.9, 1.1, 2.2 ,6.5 nm from bottom up; and of gold shelled silver (b), with core diameter of 27.2 nm, and shell thicknesses of 0, 2.2, 3.0, 4.6, 7.2, 9.0 nm from bottom up. Figure is taken from reference. ⁵⁰	17
Figure 2.8 Calculated extinction spectrums for core-shell structure, (a) dielectric ($n=3.16$) as core, with core diameter of 4 nm, and Na as shell, thickness increasing from 0.2 nm (front) to 18 nm (back); (b) Na as core, dielectric as shell, thicknesses are the same as in (a). Figure is taken from reference. ¹⁶	18
Figure 2.9 An initial estimator of performance for small metallic nanoparticle's wavelength selectivity. Definition of η is given in text. Figure is taken from reference. ¹³	20
Figure 2.10 Calculated cross-sections of scattering and absorption for Silica@Ag (core@shell) nanoparticles (embedding medium has a refractive index of 1.44). And optimizations are performed for them to scatter monochromatic light at (a, blue) $\lambda_0=458\text{nm}$, (b, green) 532nm, and (c, red) 640nm. Relative sizes of the structures are shown by insets; r denotes the outer radius of the particle. Figure is taken from reference. ¹³	22
Figure 2.11 Characterization of the transparent projection film made by dispersing Ag nanospheres with average diameter of 62 nm in PVA. (a) Comparison of the measured	

and theoretically calculated transmittance spectrums; width of the experimentally measured curve stands for one standard deviation over different wavelength of incident light. Inset is a TEM image of the Ag nanospheres with average diameter of 62 ± 4 nm. Scale bar of the TEM image is 200 nm. (b) Comparison of extinction spectrums from experimental measurement and theoretical calculation, theoretically calculated scattering and absorption are also shown. (c) Angular distribution of light scattering at the wavelength of 458 nm, with electric field of the normally incident light polarized parallel (p) and perpendicular (s) to the scattering plane. Figure is taken from reference.¹³ 24

Figure 2.12 The transparent projection display in work (left) compared with a normal piece of glass (right). A blue MIT icon is projected onto both the transparent projection display and the normal glass by a laser projector (MicroVision SHOWWX+, wavelength of blue light is 458 ± 2 nm); the image can be clearly viewed on the transparent projection display, while not on the normal glass. They place three cups with RGB letters behind the film to intuitively demonstrates the transparency. Figure is taken from reference.¹³ 25

Figure 2.13 The proposed geometry array of Ag ellipsoids: ellipsoids are placed in a square lattice and the incident light has its electric field aligned along the major axis of the ellipsoids (i.e., TE-plane wave illumination). d is the distance among centres of two adjacent nanoparticles, while a , b , and c are the major and minor axes of the ellipsoids, respectively. Figure is taken from reference.¹⁵ 26

Figure 2.14 Initial optimization of Ag ellipsoids for selective scattering of the three basic additive colours (red, green and blue). For each basic array of Ag ellipsoids, the nanoparticles' major axis has been swept from 20 nm to 40 nm while their eccentricity is fixed to 0.96, 0.9, and 0.81 for the arrays responsible of red, green and blue light, respectively. As a comparison, values of the FOM without consideration of effect of surface scattering of conduction electrons are also shown (dashed lines). Figure is taken from reference.¹⁵ 27

Figure 2.15 Proposed unit-cell of the transparent projection display that is full-colour and almost polarization-independent achieved with Ag ellipsoid arrays. The propagation direction of the incident light is along the negative direction of the z -axis. This unit-cell repeats itself in the x - y plane along the x - and the y -axes with period $d = 100$ nm. Each unit cell consists of two replicas of each of the optimized nanoparticle array in Table 2.2, and one set is rotated by 90° to the other, with adjacent layers separated by a distance t . To ensure coupling between two adjacent layers is negligible, a minimum value of t is confirmed to be 100 nm by simulations. Figure is taken from reference.¹⁵ 28

Figure 2.16 Scattering (SCS) and absorption (ACS) cross sections calculated for the display proposed in Figure 2.15 under incident light separately of each polarization (TE and TM). Figure is taken from reference.¹⁵ 29

Figure 2.17 3D angular scattering distribution for the optimized Ag ellipsoids in Table 2.2: (left) Ag ellipsoid array for selective red light scattering, (center) Ag ellipsoid array for selective green light scattering and (right) Ag ellipsoid array for selective blue light scattering. Scale is the same for all subfigures. Figure is taken from reference.¹⁵ 29

Figure 2.18 FDTD (finite-difference time-domain) simulations showing (A) a second peak emerges when a single Ag nanocube (edge length of 90 nm) approaches a glass substrate

(index assumed to be 1.5), and the near field $ E $ plots for (B) peak 1 and (C) peak 2 of the nanocube placed on the glass substrate. The surrounding medium is air, and the white line in (B), (C) represent the interface between Ag nanocube (or Air) and the glass substrate. Figure is taken from reference. ⁶⁹	30
Figure 2.19 Simulated backward scattering spectrums with FDTD for Ag nanocubes deposited on TiO_2 with sufficient thickness (800 nm). The luminosity function is also shown to indicate that human eyes are not sensitive to blue and red light. TiO_2 's refractive index is from reference. ⁷⁰ Ag's refractive index is from reference. ³² Figure is taken from reference. ¹⁴	31
Figure 2.20 Simulated results to show TiO_2 thickness versus the blue light and red light backward scattering cross sections at peak wavelength of a Ag nanocube with edge length of 100 nm on TiO_2 . Figure is taken from reference. ¹⁴	32
Figure 2.21 (a) spectrum of backward scattering and (b) transmittance spectrum of the transparent projection display experimentally fabricated by depositing a monolayer of Ag nanocubes (edge lengths have an average value of 100 nm) on the film of TiO_2 with thickness of 110 nm. The TiO_2 film is deposited on glass substrate. The luminosity function is also shown in (a). Figure is taken from reference. ¹⁴	33
Figure 2.22 (left) A colourful image is projected onto the experimentally prepared transparent projection display, model of the projector is Epson EB-1761W, whose peak wavelengths of blue, green, and red light are at 442, 552, and 612 nm, respectively; (right) Transparency of the experimentally prepared transparent display when no image is projected. Figure is taken from reference. ¹⁴	33
Figure 3.1 Light scattering and absorption by an arbitrary particle. Figure is taken from reference. ³⁰	35
Figure 3.2 Decomposition of the total extinction spectra in dipole, quadrupole and higher modes of electronic excitations. Figure is taken from reference. ¹⁶	38
Figure 3.3 Three stages of the Mie theory's mathematical procedures to calculate scattering, absorption and extinction cross sections for a single homogeneous sphere.	38
Figure 3.4 Schematic illustration of the coordinate setup of light scattering by a nanosphere. Figure is taken from reference. ³⁰	39
Figure 3.5 Multi-shelled sphere with $r - 1$ shells. Figure is taken from reference. ³⁰	43
Figure 3.6 Schematic of Yee Cell (the bigger cube) which is the base element of the discretized space by FDTD method. The smaller cube's edge length is half of that of the bigger cube. Spatial locations of one Yee Cell's components of electric field (denoted by E_x , E_y or E_z) and magnetic field (denoted by H_x , H_y or H_z) are on the six vertices of the smaller cube as shown in figure. The edge lengths of a Yee Cell along x-, y- and z- directions do not necessarily have to be equal, but FDTD would be more numerically robust if they are equal. Figure is taken from reference. ⁸²	45
Figure 3.7 Schematic illustration of SE measurement, and physical meanings of the measured values. Figure is taken from reference. ⁹³	50
Figure 4.1 Imaginary part of the dielectric functions ($\epsilon_2(\omega)$) around 530 nm for Au, Ag, Cu and Al. Optical constants are taken from the literature. ³² Figure is taken from reference. ⁹⁷	54
Figure 4.2 (a) Efficiency (defined by $(\text{cross section})/\pi a^2$, where $a = 49$ nm) for extinction,	

- scattering and absorption, calculated by the Mie theory for the chosen target structure (core = 70 nm, shell thickness = 14 nm) as a function of wavelength. (b) The blue line represents the intensity of the scattered light at the resonant wavelength (525 nm) plotted against the scattering angle (degrees) in polar form, assuming that the incident light has a unit intensity, and equal components for the p- and s-polarization with respect to the scattering plane. Calculations were done according to the Mie theory. Figure is taken from reference.⁹⁷ 58
- Figure 4.3** TEM images of Ag@TiO₂ nanoparticles with an average core diameter of 67 nm, average shell thickness of 18 nm. (a) shows a single particle of such a core-shell structure. In (b), free TiO₂ are observed. Figure is taken from reference.⁹⁷ 59
- Figure 4.4** Transmittance of the Ag@TiO₂-dispersed PVA film normalized to the pure PVA film, having an average value of 60.38%. The inset shows the comparison of the transmittance between the Ag@TiO₂-dispersed PVA film and the pure PVA film. Figure is taken from reference.⁹⁷ 61
- Figure 4.5** Comparison between measured (red) and calculated (black) extinction spectrums, and components for absorption, and forward and backward scattering calculated by Mie's theory in (a), and those derived from experimental measurements in (b). Note that the sum of the areas of forward and backward scattering gives the total scattering. The way to calculate forward and backward scattering with the Mie theory is to integrate the scattering light power from 0° to 90° and from 90° to 180° with respect to the scattering angle, respectively. The derivation of absorption, and forward and backward scattering from experimental measurements is described in Section 4.5 "Method". The parameters used in the calculations are given in the text. Figure is taken from reference.⁹⁷ 62
- Figure 4.6** (a) Demonstration of the transparent nanoparticle-dispersed PVA film which selectively scatters green light. (b) A pure PVA film without nanoparticles is shown for comparison. The images were projected by a laser projector (SONY MP-CL1A). The images of (a) and (b) are captured with the same lighting and exposure conditions, and the photographs have not been edited. Figure is taken from reference.⁹⁷ 64
- Figure 4.7** (a) Efficiency (defined by (cross section)/ πa^2 , where $a = 76.5$ nm) for extinction, scattering and absorption, calculated by the Mie theory for the structure with the highest FOM (core = 75 nm, shell thickness = 39 nm) as a function of wavelength. (b) The blue line represents the intensity of the scattered light at the resonant wavelength (620 nm) plotted versus the scattering angle (degrees) in polar form, assuming incident light has a unit intensity, and equal components for the p- and s-polarization with respect to the scattering plane. Calculations are done with the Mie theory. Figure is taken from reference.⁹⁷ 66
- Figure 4.8** Experimental setup to obtain a film's transmittance, extinction, absorption, scattering, ratio of forward and backward scattering values employing an integrating sphere. The directly measured values are $T_1(\lambda)$, $T_2(\lambda)$, $T_3(\lambda)$, $T_4(\lambda)$, $T_5(\lambda)$ and $R(\lambda)$ where T_i ($i = 1,2,3,4,5$) or $R(\lambda)$ is proportional to the amount of light trapped in the integrating sphere. The transmittance, extinction, absorption, scattering, ratio of forward and backward scattering values are deduced from these measured values. Figure is taken from reference.⁹⁷ 67
- Figure 4.9** Schematic showing light attenuation when going through a thin film. $I_1\lambda$ denotes

the incident light intensity. $I_{2\lambda}$ denotes the intensity for the light propagating in the original direction after a loss from $I_{1\lambda}$ at the left air / film boundary due to reflectance and surface scattering. $I_{3\lambda}$ denotes the intensity for the light propagating in the original direction after a loss from $I_{2\lambda}$ due to scattering and absorption during the course from the left air / film boundary to the right film / air boundary. $I_{4\lambda}$ denotes the intensity for the light propagating in the original direction after a loss from $I_{3\lambda}$ at the right film / air boundary due to reflectance and surface scattering. Figure is taken from reference.⁹⁷

..... 68

Figure 5.1 Calculated extinction and absorption efficiencies with and without consideration of surface scattering of conduction electrons, where Q_{ext} stands for extinction efficiency, and Q_{abs} stands for absorption efficiency. The scattering efficiency is the difference between the Q_{ext} and Q_{abs} . All calculations are carried out by Mie theory, with Silica and surrounding medium's indices assumed to be 1.45 and 1.5 respectively. Au's dielectric constants without surface scattering is from reference,³² while that with surface scattering is given by equations (5.1)~(5.3). (a) is for (80 nm diameter Silica core)@(15 nm thickness Au shell); (b) is for (80 nm diameter Silica core)@(25 nm thickness Au shell); (c) is for (80 nm diameter Silica core)@(35 nm thickness Au shell); and (d) is for (80 nm diameter Silica core)@(45 nm thickness Au shell). Figure is adapted from reference.⁶¹

77

Figure 5.2 E_2 plots of the four structures shown in Figure 5.1 at their corresponding dipolar resonance peak wavelengths. (a) and (b) are plotted for (80 nm diameter Silica core)@(15 nm thickness Au shell) at 700 nm; (c) and (d) are plotted for (80 nm diameter Silica core)@(25 nm thickness Au shell) at 684 nm; (e) and (f) are plotted for (80 nm diameter Silica core)@(35 nm thickness Au shell) at 706 nm; (g) and (h) are plotted for (80 nm diameter Silica core)@(45 nm thickness Au shell) at 756 nm. Left column, i.e., (a), (c), (e) and (g) show E_2 calculated with bulk Au's dielectric constants from reference.³² Right column, i.e., (b), (d), (f) and (h) show E_2 calculated with Au's dielectric constants modified with surface scattering via equations (5.1)~(5.3). The polarization and the propagating direction of the incident light are same for all figures and are shown in (a). Figure is taken from reference.⁶¹

79

Figure 5.3 TEM images of the three Au nanoshells used in experimental measurements. (a) 80 nm diameter Silica core, 16 nm thickness Au shell, (b) 79 nm diameter Silica core, 29 nm thickness Au shell, (c) 88 nm diameter Silica core, 36 nm thickness Au shell. The detailed characterization information is provided in Appendix A. Figure is taken from reference.⁶¹

..... 80

Figure 5.4 Comparisons between measured and calculated absorption spectrums with and without consideration of surface scattering of conduction electrons. All calculations are carried out by Mie theory. The surrounding medium is PVA (polyvinyl alcohol) having a refractive index of 1.5. The surfactants coating the nanoshells can be neglected because the surfactants are thin polymer and have similar refractive index as the surrounding medium of PVA. The refractive index of Silica is assumed to be 1.45 in the calculations. Au's dielectric constants without surface scattering is from reference,³² while that with surface scattering is given by equations (5.1) and (5.4). In all figure legends, "Ext" is short for extinction, "Abs" is short for absorption, and "SC" is short for surface

- scattering. In each figure, “Ext calculated”, and “Abs calculated with SC” are the extinction and absorption spectrums calculated with the fitting parameters shown in Table 5.2, while “Abs calculated without SC” is the absorption cross section calculated without considering size distribution and surface scattering. (a) (80 nm diameter Silica core)@(16 nm thickness Au shell), (b) (79 nm diameter Silica core)@(29 nm thickness Au shell), and (c) (88 nm diameter Silica core)@(36 nm thickness Au shell). Figure is taken from reference.⁶¹ 81
- Figure 5.5** (a) Film dispersed with 16-nm Au nanoshell. (b) Film dispersed with 29-nm Au nanoshell. (c) Film dispersed with 36-nm Au nanoshell. (d) Pure PVA film. Figure is taken from reference.⁶¹ 86
- Figure 5.6** Experimental Setup to measure absorption. The directly measured values are $T_1(\lambda)$, $T_2(\lambda)$ and $R(\lambda)$ where T_i ($i = 1, 2$) or $R(\lambda)$ is proportional to the amount of light trapped in the integrating sphere. The absorption is deduced from these measured values. This setup is a simplified version of the one reported in Section 4.5. Figure is taken from reference.⁶¹ 88
- Figure 6.1** Calculated extinction efficiency spectrum of a single nanosphere with diameter of 10 nm by Mie theory,³⁰ for (a) Ag, (b) Au and (c) Al. The real part of dielectric function is plotted for (d) Ag, (e) Au and (f) Al. The surrounding medium’s refractive index is 1.5, so surrounding medium’s dielectric function is 2.25, and the resonance peaks appear at the wavelengths at which real part of metals’ dielectric function equal to -4.5. The dielectric functions of the metals are from literature.³² Figure is taken from reference.¹⁸ 94
- Figure 6.2** Schematic illustration of the structures to be used during optimization, where metal refers to Ag, Au or Al. The surrounding medium’s refractive index is assumed to be 1.5. (a) A single metallic nanosphere. (b) The core-shell structure of “Silica@Metal” without gain material. (c) The core-shell structure of “Metal@Silica”, Silica shell is doped with gain material. (d) The core-shell structure of “Silica@Metal”, Silica core is doped with gain material. Figure is adapted from reference.¹⁸ 96
- Figure 6.3** Efficiency spectrums of optimized structures for selective scattering of red light. The left column, i.e., (a), (c), (e) and (g) are for the optimized structures without gain material, and spectrums of their corresponding structures optimized with gain material are shown in the right column, i.e., (b), (d), (f) and (h). (a) Au sphere without gain. (b) Au@Silica with gain. (c) Silica@Au without gain. (d) Silica@Au with gain. (e) Silica@Ag without gain. (f) Silica@Ag with gain. (g) Silica@Al without gain. (h) Silica@Al with gain. For each structure, the optimized parameters and optimized values of FOM are tabulated in Table 6.3 in the same alphabetic order as their respective structure appears in this figure. Figure is taken from reference.¹⁸ 102
- Figure 6.4** Efficiency spectrums of optimized structures for selective scattering of green light. The left column, i.e., (a), (c) and (e) are for the optimized structures without gain material, and spectrums of their corresponding structures optimized with gain material are shown in the right column, i.e., (b), (d) and (f). (a) Ag sphere without gain. (b) Ag@Silica with gain. (c) Silica@Ag without gain. (d) Silica@Ag with gain. (e) Silica@Al without gain. (f) Silica@Al with gain. For each structure, the optimized parameters and optimized values of FOM are tabulated in Table 6.4 in the same alphabetic order as their

- respective structure appears in this figure. Figure is taken from reference.¹⁸103
- Figure 6.5** Efficiency spectrums of optimized structures for selective scattering of blue light. The left column, i.e., (a), (c) and (e) are the optimized structures without gain material, and spectrums of their corresponding structures optimized with gain material are shown in the right column, i.e., (b), (d) and (f). (a) Ag sphere without gain. (b) Ag@Silica with gain. (c) Silica@Ag without gain. (d) Silica@Ag with gain. (e) Silica@Al without gain. (f) Silica@Al with gain. For each structure, the optimized parameters and optimized values of FOM are tabulated in Table 6.5 in the same alphabetic order as their respective structure appears in this figure. Figure is taken from reference.¹⁸104
- Figure 6.6** Intensity of the scattered light at the resonant wavelengths versus the scattering angle (in the unit of degree) in polar form for the most suitable structures respectively for selective scattering of red, green and blue light: (a) Silica@Au with gain material (Table 6.3), (b) Silica@Ag with gain material (Table 6.4), and (c) Ag@Silica with gain material (Table 6.5). The incident light has a unit intensity and equal intensity for the p- and s-components with respect to the scattering plane. Calculations are carried out with the Mie theory. Figure is taken from reference.¹⁸107
- Figure 6.7** Simulated transmittance of a film dispersed with the three most suitable structures. Densities of the three structures are chosen such that transmittance at their corresponding resonance wavelengths become 20%. Surrounding medium is assumed to have a refractive index of 1.5. Average transmittance is 60.66%. Figure is taken from reference.¹⁸108
- Figure 6.8** Efficiency spectrums recalculated for the three most suitable structures, (a) Silica@Au with gain material (corresponding to Figure 6.3 (d)) for red light, (b) Silica@Ag with gain material (corresponding to Figure 6.4 (d)) for green light, and (c) Ag@Silica with gain material (corresponding to Figure 6.5 (b)) for blue light, with gaussian-form k , which is described by equation (6.6).110
- Figure 7.1** FDTD simulation to show when a Ag nanocube (90 nm edge) in air approaches a dielectric substrate (glass), the single scattering peak splits into two. Formation of D and Q modes is explained in text and by Figure 7.3. Figure is adapted from reference.⁶⁹114
- Figure 7.2** Normalized surface charge distributions for the bright dipolar plasmon mode D^0 (left), and the dark quadrupolar plasmon mode Q^0 (right). Figure is adapted from reference.¹⁶⁹115
- Figure 7.3** (a) When a Ag nanocube is placed on a dielectric substrate, charges will be induced in the substrate by D^0 and Q^0 modes, and this induced charge mediate D^0 and Q^0 hybridization. (b) An illustration of charge distributions when D^0 and Q^0 modes are fully hybridized, and the forming of the bonding D and antibonding Q modes: $D = D^0 + Q^0$ and $Q = D^0 - Q^0$. (c) Energy diagram demonstrating the effect of dielectric substrate: pure dielectric screening effect (black dashed line) causing red shifts of both D^0 and Q^0 modes and the substrate-mediated hybridization (blue thin line) which leads to the bonding D and antibonding Q modes. Figure is adapted from reference.¹⁶⁹116
- Figure 7.4** Scattering cross sections (in nm^2) calculated for Ag nanocube with edge length of 100 nm in three setups: without dielectric substrate (solid red line), with TiO_2 substrate and light incident from air to TiO_2 (dashed green line), with TiO_2 substrate and light

- incident from TiO₂ to air (dashed blue line). Insets illustrate the propagation direction and polarization of light. Figure is taken from reference.¹⁷⁴117
- Figure 7.5** (a) Forward and backward components of scattering cross section of 100-nm Ag nanocube placed on TiO₂ substrate, with the light propagation direction (Air-to-TiO₂) and polarization illustrated by the inset. (b) Near electric field amplitude $|E|$ spatial plot at Peak I (wavelength = 435 nm) as indicated in (a). (c) Near electric field amplitude $|E|$ spatial plot at Peak II (wavelength = 710 nm) as indicated in (a). The white dotted line in (b) and (c) indicates the Air/TiO₂ interface. The plane at which amplitude of electric field is recorded is parallel to paper and is placed 1 nm away from the front face of Ag nanocube. Figure is taken from reference.¹⁷⁴119
- Figure 7.6** (a) Forward and backward components of scattering cross section of 100-nm Ag nanocube placed on TiO₂ substrate, with light propagation direction (TiO₂-to-Air) and polarization illustrated by the inset. (b) Near electric field amplitude $|E|$ spatial plot at Peak I (wavelength = 440 nm) as indicated in (a). (c) Near electric field amplitude $|E|$ spatial plot at Peak II (wavelength = 710 nm) as indicated in (a). The white dotted line in (b) and (c) indicates the Air/TiO₂ interface. The plane at which amplitude of electric field is recorded is parallel to paper and is placed 1 nm away from the front face of Ag nanocube. Figure is taken from reference.¹⁷⁴120
- Figure 7.7** Simulated forward scattering cross sections for TiO₂-substrate/Ag nanocubes are shown in (a) and (b), and for glass-substrate/Au nanocubes are shown in (c) and (d). Incident direction and polarization of light for each sub-figure are illustrated by its corresponding inset. Figure legends denote the edge lengths of nanocubes. For all simulations shown in this figure, a 2-nm gap between the bottom of nanocube and the dielectric substrate is assumed to simulate the protective reagent in a real situation,¹⁴ such as PVP (Polyvinyl Pyrrolidone). The scale of the vertical axis is the same for all sub-figures for easy comparison. Figure is taken from reference.¹⁷⁴121
- Figure 7.8** Simulated backward scattering cross sections for TiO₂-substrate/Ag nanocubes are shown in (a) and (b), and for glass-substrate/Au nanocubes are shown in (c) and (d). Incident direction and polarization of light for each sub-figure are illustrated by its corresponding inset. Figure legends denote the edge lengths of nanocubes. For all simulations shown in this figure, a 2-nm gap between the bottom of nanocube and the dielectric substrate is assumed to simulate the protective reagent in a real situation,¹⁴ such as PVP (Polyvinyl Pyrrolidone). The scale of the vertical axis is the same for all sub-figures for easy comparison. Figure is taken from reference.¹⁷⁴122
- Figure 7.9** Calculated scattering cross sections of TiO₂ substrate/Au nanocube of different sizes. (a) Light is incident from air to TiO₂, and (b) light is incident from TiO₂ to air. Insets show the schematics for the two setups. Legends indicate the edge lengths of Au nanocubes. It is observed that when resonance peak wavelengths are smaller than 700 nm, scattering cross sections of TiO₂ substrate/Au nanocubes are smaller than $5 \times 10^4 \text{ nm}^2$, which is too small compared to those of glass substrate/Au nanocubes, but by increasing Au nanocube's size to increase its scattering cross section, its peak wavelength is beyond 700 nm, for both setups of Air-to-TiO₂ and TiO₂-to-Air as shown in (a) and (b). And forward and backward scattering cross sections are even smaller when resonance peak wavelength is smaller than 700 nm, since scattering cross section is the sum of these two.

Figure is taken from reference. ¹⁷⁴	124
Figure 7.10 Combined overall forward or backward scattering cross sections for the three combinations discussed in text, with their schematics shown by insets, and effect of TiO ₂ thin film's thickness and light reflections at all interfaces are considered for all three combinations. (a) Overall backward scattering for the first combination combined from those of Ag nanocube and Au nanocube, thickness of the TiO ₂ thin film is 137 nm. (b) Overall forward scattering for the second combination combined from those of Ag nanocube and Au nanocube, thickness of the TiO ₂ thin film is 100 nm. (c) Overall forward scattering as well as backward scattering for the third combination combined from that of Ag nanocube at the foreside and that of Ag nanocube at the back side, thickness of both the two TiO ₂ thin films is 120 nm. In (a), (b) and (c), Ag nanocube's edge length is 120 nm. In (a) and (b), Au nanocube's edge length is 130 nm. For all simulations shown in this figure, a 2-nm gap between the bottom of nanocube and the dielectric substrate is assumed to simulate protective reagent in a real situation, ¹⁴ such as PVP (Polyvinyl Pyrrolidone). Figure is taken from reference. ¹⁷⁴	128
Figure 7.11 Normalized scattering intensity $ E ^2$ plotted versus scattering angle for the three combinations shown in Figure 7.10. (a) Plotting for the first combination at the wavelength of 455 nm. (b) Plotting for the first combination at the wavelength of 680 nm. (c) Plotting for the second combination at the wavelength of 460 nm. (d) Plotting for the second combination at the wavelength of 680 nm. (e) Plotting for the third combination at the wavelength of 460 nm. (f) Plotting for the third combination at the wavelength of 685 nm. All scattering intensities shown in this figure consist of contributions from both the nanocubes placed on the foreside and backside of the TiO ₂ -coated glass slide. Incident light has equal components for s- and p- polarisations with respect to the scattering plane. Each sub-figure's angular distribution of scattering intensity is normalized to its largest value. Figure is taken from reference. ¹⁷⁴	130

List of Tables

Table 2.1 Optimized size parameters of particle and FOM for spherical core-shell structure of Silica@Ag. Table is adapted from reference. ¹³	23
Table 2.2 Optimal particle sizes and FOM for ellipsoidal Ag nanoparticles.....	28
Table 4.1 Optimization results. The optimization starts with an initial guess of the shell thickness at each quantized diameter value. Table is adapted from reference. ⁹⁷	59
Table 5.1 Comparison of the absorption ratio between the calculations with and without the surface scattering effect of conduction electrons. The results are obtained from Figure 5.1. Table is taken from reference. ⁶¹	78
Table 5.2 Values of the fitting parameters for the calculated spectrums shown in Figure 5.4. Table is taken from reference. ⁶¹	83
Table 6.1 Structures on which optimizations are to be performed to search for solutions of sharp selective scattering of red, green and blue light. Table is taken from reference. ¹⁸	96
Table 6.2 Plasma frequencies, damping rates and Fermi velocities of bulk metals used in correcting the metals' dielectric functions for the size effect. Table is taken from reference. ¹⁸	98
Table 6.3 Optimized tuning parameters and values of optimized FOM for the structures mentioned in Figure 6.3, with the same alphabetic order. Table is taken from reference. ¹⁸	100
Table 6.4 Optimized tuning parameters and values of optimized FOM for the structures mentioned in Figure 6.4, with the same alphabetic order. Table is taken from reference. ¹⁸	100
Table 6.5 Optimized tuning parameters and values of optimized FOM for the structures mentioned in Figure 6.5, with the same alphabetic order. Table is taken from reference. ¹⁸	101
Table 6.6 Comparison of optimized values of FOM from this work to those from previous works for red, green and blue light. Table is taken from reference. ¹⁸	106

Nomenclatures

LSPR	Localized Surface Plasmon Resonance
Ag	Silver
Au	Gold
Al	Aluminum
ε	Dielectric function of a material
ε_1	Real part of dielectric function of a material
ε_2	Imaginary part of dielectric function of a material
ω	Angular frequency of incident light
λ	Wavelength of incident light
σ_{ext}	Extinction cross section in nm ²
σ_{abs}	Absorption cross section in nm ²
σ_{sca}	Scattering cross section in nm ²
Q_{ext}	Extinction efficiency, defined in Section 3.1
Q_{abs}	Absorption efficiency, defined in Section 3.1
Q_{sca}	Scattering efficiency, defined in Section 3.1
c	Speed of light
ε_m	Dielectric function of surrounding medium
λ_0	Resonant wavelength of LSPR
DDA	Discrete Dipole Approximation
FDTD	Finite Difference Time Domain
A@B	Spherical core A, coated with concentric Spherical Shell B
SERS	Surface Enhanced Raman Scattering
η	Performance estimator of metal (See Figure 2.9)
FOM	Figure of Merit, defined by Equation (2.6)
PVA	Polyvinyl Alcohol, a transparent polymer matrix
IPA	Isopropanol, a solvent
N (Chapter 3)	Material's complex refractive index
n	Material's refractive index, real part of N
k	Material's extinction coefficient, imaginary part of N

ε_{sh} (Chapters 4,5)	Dielectric function of shell material of a core-shell structure
ε_C (Chapter 4)	Metal's dielectric function corrected with size effect
TEM	Transmission Electron Microscope
N (Chapter 5)	Areal density of nanoparticle
N (Chapter 6)	Volumetric density of nanoparticle
N' (Chapter 6)	Areal density of nanoparticle

Chapter 1. Introduction

1.1 Background and Motivation

A transparent display enables us to see both the image displayed on it and the view behind it. Therefore, transparent display finds applications in, for example, virtual reality (VR) or augmented reality (AR), which appears to show a floating object in air, and shop windows that can show translucent images and movies for advertisement purpose, and head up display which shows navigation information in a car's window shield. The market of Head Up Display is expected to be worth 4.71 Billion USD by 2023.¹ And the market size of VR/AR is expected to hit 209 billion USD by 2022.²

Several types of transparent displays have been studied, each has its own advantages and disadvantages. The most popular transparent projection display is the microlens array (MLA) based displays, it can achieve high colour saturation and high resolution depending on the material employed.³⁻⁴ However, since it works by reflecting the image off a beam splitter and projecting into the viewer's eyes, this type of display suffers from the problem of viewing angle and fabrication complexity.⁵ Diffusive display is made by dispersing high-refractive particles such as TiO_2 or nano-diamond in a visibly transparent matrix.⁶⁻⁷ The fabrication is simple for diffusive display, and achieves wider angles of viewing compared to MLA based displays, but it suffers from a trade-off between projected image clearness and transparency since the scattering is rather uniform for all wavelengths of visible light. In the case of projection-based fluorescent display, three thin layers separately containing fluorescent materials emitting red green and blue light upon absorbing their corresponding excitation light are stacked.⁸ The projection-based fluorescent display may have a potential to achieve satisfying transparency as well as the displayed image contrast ratio, but it must employ a specially designed projector that generates excitation wavebands. An active solution of transparent display is enabled by Organic light emitting diode (OLED): OLED based

display is made by combining OLED and transparent electrodes such as indium tin oxide (ITO).⁹⁻¹⁰ Despite the cost of OLED based display can be theoretically reduced by screen printing,¹¹ and its advantage in flexibility, it suffers from the limited lifetime of the organic materials,⁹ and susceptibility to water damage.¹² So, it is of interest to search for a way to overcome the shortages of existing solutions.

Recently, the idea of selective scattering of red, green and blue light and transmission of visible light of other colours to achieve transparent projection display has been proposed,¹³⁻¹⁵ which takes advantage of metallic nanoparticle's localized surface plasmon resonance (LSPR),¹⁶⁻¹⁷ and is schematically shown in Figure 1.1. This approach relies on special engineering of metallic nanoparticles such that when they are embedded in a transparent matrix, they only selectively scatter red, green and blue light and transmit the visible light of other colours. This approach is scalable to large display sizes, can ensure image clearness and transparency by frequency-selective of light scattering, and has large viewing angle as will be demonstrated later in this thesis.

Figure 1.1 Schematic illustration of the concept of transparent projection display achieved by selective scattering of red, green and blue light. This demonstrates the ideal case: light scattering spectrums have ultra-sharp peaks around wavelengths of the three primary colours (red, green and blue), while light absorption remains 0 all through the visible light wavelength range. Figure is taken from reference.¹⁸

At the beginning of my PhD's work (year 2015), little research had been dedicated to transparent projection display based on metallic nanoparticle's LSPR (selective scattering enhancement had been experimentally demonstrated only for blue light,¹³⁻¹⁴ simulating studies were also very limited), and this forms the motivation of the subsequent efforts reported in this thesis.

1.2 Objective and Scope of research

Since little research has been dedicated to engineering of metallic nanoparticle to achieve selective scattering of red, green and blue light, many problems remain unsolved:

- 1) Scattering peak width (the narrower, the better the frequency-selectivity) from reported works¹³⁻¹⁵ are too broad compared to the ideal case shown in Figure 1.1.
- 2) Experimental realizations for green and red light have not been demonstrated: the theoretical designs proposed in references^{13, 15} are not easy to synthesize.
- 3) Light absorption in proposed designs¹³⁻¹⁵ are still high compared to the ideal case shown in Figure 1.1 which has 0 absorption all through the visible wavelength range.

So, the objective of this thesis is to attempt to solve the above problems, by studying light scattering and absorption properties based on metallic nanoparticles' LSPR, and proposing new designs.

The scope of this research focuses on design or prediction of light scattering and absorption behaviours of metallic nanoparticles by numerical simulations, followed by some experimental verifications. Thus, chemical synthesis of nanoparticles is not the focus of this thesis. Simulation methods, as well as experimental verification methods will be discussed later in the Chapter "Methodology".

1.3 Major Contributions of the thesis

This thesis has studied light scattering and absorption properties of different nanostructures with silver (Ag) or gold (Au) as constituent materials. Nanostructures studied include spherical core-shell structures of Ag@TiO₂ (Core@Shell), Silica@Au (i.e., gold nanoshell), Silica@Ag, Ag sphere, Au sphere, Ag@Silica, Au@Silica, Ag Nanocube and Au Nanocube. This thesis has also studied the possibility of achieving sharp light scattering peak (i.e., high frequency-selectivity) and low absorption of light by combining Ag or Au nanoparticles with gain materials. Detailed descriptions of contributions are listed below:

- 1) Design and optimization of core diameter and shell thickness of the structure of Ag@TiO₂ to achieve selective scattering of green and red light has been carried out. Experimental verification of selective scattering of green light was realized. And I am the first one to realize selective scattering of green light experimentally.
- 2) Effect of surface scattering of free electrons in nanoparticles on ratio of optical scattering and absorption has been investigated. Since nanoparticle's size is comparable to free electrons' mean free path in the corresponding constituent material, more collisions of electrons on metal/dielectric interface are expected (this process is referred to as surface scattering of free electrons). Simulation of Au nanoshell's (Silica@Au) optical scattering and absorption were conducted with and without consideration of surface scattering to predict its effect on light scattering and absorption. Experimental verification results qualitatively agree with those from simulation prediction. Both results from simulation and experiments indicate that surface scattering of free electrons increases light absorption, decreases light scattering and broadens the width of scattering peak.
- 3) Numerical simulations are performed on nanostructures based on Ag, Au or aluminium (Al) with or without gain material, to examine the effect of gain and to search for suitable structures for sharp selective scattering of red, green and blue light. It is found that including gain material greatly improves the performance for

structures based on Ag or Au, but not for structures based on Al. The most suitable structures for sharp selective scattering of red, green and blue light are respectively found to be Silica@Au, Silica@Ag and Ag@Silica, with all three structures' Silica doped with gain material.

- 4) Through numerical simulation, forward and backward scattering properties of dielectric substrate/Ag (or Au) nanocube structures are investigated. And based on these properties, three designs, which can achieve selective scattering of blue and red light in forward or backward or both directions, are proposed.

1.4 Organization of the thesis

The chapters of this thesis are organized as following:

In Chapter 1, background of transparent displays is introduced, followed by a brief review of existing solutions for transparent display. Then the idea and unsolved problems of transparent projection display based on metallic nanoparticle's LSPR are presented, leading to the motivation and objective of this thesis. Finally, major contributions of this thesis are summarized.

In Chapter 2, firstly, interesting properties of LSPR are reviewed, including effects of constituent material's dielectric function of a particle, particle's size, surrounding medium's refractive index, particle's shape and a coating shell on the resonance peak's position and width. Secondly, LSPR's applications are reviewed.

In Chapter 3, methods employed during the research are described. Firstly, two simulation methods, the Mie theory and Finite-Difference Time-Domain, are reviewed. After that, Spectroscopic Ellipsometry, a method to measure material's refractive index is briefly reviewed.

In Chapter 4, selective scattering of green and red light based on the structure of

Ag@TiO₂ is presented. The reason of choosing this structure is given, followed by theoretical optimization of structural parameters to realize selective scattering of green and red light. The designed nanoparticle's ability to selectively scatter green light is verified experimentally by characterization of a transparent film produced by dispersing such nanoparticles in a polymer matrix

In Chapter 5, the effect of surface scattering of electrons on the ratios of optical absorption and scattering to extinction (which is the sum of the absorption and scattering) of gold nanoshell is investigated. Both simulations and experimental verifications are conducted for several shell thicknesses, followed by analysis and discussion.

In Chapter 6, possibility of achieving sharp light scattering peak (i.e., high frequency-selectivity) and low absorption of light by combining metallic nanoparticles with gain material is investigated. Systematic numerical simulations are performed on nanostructures based on Ag, Au or aluminium (Al) with or without gain, followed by analysis and discussion.

In Chapter 7, light scattering properties of Ag and Au nanocubes placed on dielectric substrate are investigated through numerical simulations. Based on these properties, the potential of using Ag and Au nanocubes to achieve selective scattering of blue and red light is discussed.

In Chapter 8, the research works carried out in this thesis are summarized. Some recommendations for future work are discussed.

Chapter 2. Literature review

Localized surface plasmons (LSPs) are characterized by free electron cloud oscillations (Figure 2.1)¹⁷ confined to metallic nanoparticles (or referred to as metal clusters) and nanostructures induced by illuminating electromagnetic field.¹⁶ Although localized surface plasmons effect can also be found in doped semiconductors and semimetals,¹⁹⁻²² it is most prominent in metals. For free electron metals like the alkalis, the oscillating electron cloud mainly consists of free electrons experiencing transitions within the conduction band. Whereas in other metals, the oscillating electron cloud has a substantial portion of electrons experiencing transition from lower-lying bands into the conduction band or from the conduction band into higher unoccupied levels. Noble metals like Au, Ag and copper (Au) show both types of electrons in its oscillating electron cloud when exposed to electromagnetic field of appropriate frequencies.²³⁻²⁴ The localized surface plasmons resonance (LSPR) effect happens when the incident electromagnetic field has a frequency that induces a peak (or a local maximum) extinction (scattering + absorption of incident light) strength of the nanoparticle, accompanied by an enhanced local electromagnetic field near the nanoparticle's surface. The light extinction, scattering and absorption strengths are characterized by their respective cross sections, which can be intuitively perceived as the area amount of light removed from the path of incident light due to scattering, absorption, or extinction respectively and are defined by the ratio of corresponding power losing rates (i.e. extinction, scattering and absorption) to the intensity of the incoming illuminating electromagnetic field.²⁵ A more detailed explanation of these cross sections is in Section 3.1: "Methods for simulating nanoparticle's light scattering and absorption". The wavelength, width, and the strength of the resonant extinction spectrum peak are characteristic of the nanoparticle's material type in the form of dielectric function, size, type of surrounding medium and shape.^{16-17, 26-27}

Figure 2.1 Electron cloud oscillation, showing the relative displacement of electrons to the nuclei induced by illuminating electromagnetic field. Figure is taken from reference.¹⁷

In this chapter, the effects of metallic nanoparticle's dielectric function, size, refractive index of surrounding medium and particle shape on the wavelength, width, and the strength of the extinction spectrum's resonant peak(s) are qualitatively described. A brief review of some common applications of metallic nanoparticle's LSPR is given, followed by a detailed review of existing solutions of transparent projection display based on metallic nanoparticle's LSPR.¹³⁻¹⁵

2.1 General properties of LSPR

A. Effect of metallic nanoparticle's dielectric function

Different types of material have different reactions to incident electromagnetic fields, and these different reactions are described by the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, which is a function of incident electromagnetic field's frequency. Under the condition that the metallic nanoparticle's size is very small ($<10\text{nm}$), the dielectric function is also dependent on its size.²⁸ For metals, their dielectric function generally can be described by the Drude-Lorentz Model,²⁹ with the free electron behaviour accounted for by the Drude component, and the interband transitions of bound electrons accounted for by the Lorentz components. To qualitatively understand the effect of material's dielectric function on the nanoparticle's resonant peak, it is convenient to assume the quasi-static approximation and the particle to be spherical. The strict criteria

of quasi-static regime for nanoparticles is $R/\lambda \leq 0.01$, where R is the radius of the nanoparticle.¹⁶ Compared to the full exact calculation given by Mie's theory,³⁰ which is reviewed in Chapter 3, the generally multipolar excitations are restricted to the dipolar electric mode, or dipolar electric mode dominates. In addition, under the assumption of quasi-static approximation, phase shifts, also called the retardation effects of the electromagnetic field over the nanoparticle are negligible (Figure 2.2)¹⁶. In other words, under quasi-static approximation, the electromagnetic field is dependent on time but not on space, and the sphere feels a field with a spatially constant phase.

Figure 2.2 Assuming quasi-static approximation, the sphere feels a spatially constant phase of incident electromagnetic field, as compared to the general case. Figure is adapted from reference.¹⁶

Under quasi-static approximation, the extinction cross section can be derived and is given below:¹⁶

$$\sigma_{ext}(\omega) = 9 \frac{\omega}{c} \varepsilon_m^{3/2} V \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2} \quad (2.1)$$

where ω is the incident electromagnetic wave's frequency, c is the speed of light, $V = (4\pi/3)R^3$ denotes the particle's volume, ε_m is the dielectric function of the embedding medium, and $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the dielectric function of the particle material. From equation (2.1), it is obvious that the resonant wavelength corresponds to the frequency ω that makes the denominator $[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2$ take its minimum. And this simplifies to:

$$\varepsilon_1(\omega) = -2\varepsilon_m \quad (2.2)$$

provided that $\varepsilon_2(\omega)$ is small or does not change much near the resonance.

As for the width of the resonance peak, it is determined by the damping experienced by the oscillation electrons, i.e. scattering of electrons at phonons, lattice defects, impurities, etc. The expression for width Γ^* (in eV) is derived in reference and given below:³¹

$$\Gamma^* = \frac{2\varepsilon_2}{\sqrt{\left(\frac{d\varepsilon_1}{d\omega}\right)^2 + \left(\frac{d\varepsilon_2}{d\omega}\right)^2}} (1 + \beta) \quad (2.3)$$

where $\beta(\omega_{resonance}, \varepsilon_2, d\varepsilon_1/d\omega, d\varepsilon_2/d\omega) \leq 10^{-3}$ for the case of Ag nanoparticle.

The derivatives are taken at $\omega = \omega_{resonance}$.

The width of the resonance peak quantitatively shows sharpness of this peak. An alternative way to show sharpness of a peak is given by calculating the ratio between scattering cross section of on-resonance (at resonant wavelength λ_0) and scattering cross section of off-resonance (at $\lambda_0 + \Delta\lambda$, for a small wavelength step $\Delta\lambda$):¹³

$$\frac{\sigma_{sca}(\lambda_0)}{\sigma_{sca}(\lambda_0 + \Delta\lambda)} \approx 1 + \left| \frac{\varepsilon_1(\lambda_0 + \Delta\lambda) - \varepsilon_1(\lambda_0)}{\varepsilon_2(\lambda_0)} \right|^2 \quad (2.4)$$

A sharp scattering peak is equivalent to a large value of the ratio shown by left-hand-side of equation (2.4). Therefore, by observing right-hand-side of both equation (2.3) and equation (2.4), it is obvious that a small imaginary part of the metal's dielectric function or a fast-changing real part of the metal's dielectric function generates sharp resonant peak.

To show the effect of dielectric function on wavelength and width of resonant peak, full exact extinction cross sections calculated by the Mie theory for Sodium (Na), Ag, Au and Aluminium (Al) nanospheres with diameter equalling to 10 nm are given in Figure 2.3 with their dielectric functions of bulk materials plotted with the same wavelength range. From Figure 2.3, it shows that for Al, Na and Ag, $\varepsilon_2(\omega)$ is small in the vicinity

of the resonance wavelength, where $\varepsilon_1(\omega) = -2$ ($\varepsilon_m = 1$). And so, sharp resonant peaks occur at the wavelength where $\varepsilon_1(\omega) = -2$. For Au, since near the wave length of $0.5\mu m$ where $\varepsilon_1(\omega) = -2$, $\varepsilon_2(\omega)$ is neither small nor mildly changing, the resonance peak is only locally identified near the resonant wavelength. Comparing the extinction spectrums of Al, Na, Ag to that of Au, it is obvious that Au's peak locally occurred around wavelength of $0.5\mu m$ is much broader. And this can be revealed by equation (2.3) (or equation (2.4)), since $\varepsilon_2(\omega)$ in the numerator is much larger for Au than that of the other three around the four metals' respective resonant wavelength, the width of extinction peak for Au is wider than the rest.

Figure 2.3 Computed extinction cross section spectra with the Mie theory of spherical particles with diameter of 10 nm. (a) Al; (b) Na; (c) Ag; (d) Au, and their corresponding dielectric functions (a') for Al, (b') for Na, (c') for Ag and (d') for Au. Optical constants are from references.³²

A more accurate approximation of the extinction spectrum under the assumption of quasi-static condition takes into account the effect of quadrupole mode of the electrons oscillation where half of the electron cloud moves parallel to the applied field

and half moves antiparallel.¹⁷ The contribution of the quadrupole mode gives an additional term similar to that in equation (2.1), which features the quadrupole mode resonance condition:

$$\varepsilon_1(\omega) = -\frac{3}{2}\varepsilon_m \quad (2.5)$$

again, provided that $\varepsilon_2(\omega)$ is small or does not change much near quadrupole resonance.

The width of the quadrupole mode resonance peak is also described by equation (2.3).

B. Effect of metallic nanoparticle's size

Examples of Al, Na, Ag and Au are given in Figure 2.4, where the refractive index of the surrounding medium is assumed to be 1 (vacuum) for Na, Ag and Au, while assumed to be 1.33 (water) for Al. The general trends of effect of increasing size on the extinction spectrum can be summarized below:

1. When the particle is very small (diameter around 10 nm), the extinction peak is mainly due to dipole resonance, and its position can be approximated by the quasi-static derivations, i.e. equations (2.2) and (2.5).
2. When the size of the nanoparticle increases, the dipole resonance red-shifts. And higher order resonance peaks occur: quadrupole resonance peak, followed by octupole resonance peak, and so on.
3. For peaks of each mode, i.e. dipole mode, quadrupole mode, octupole mode and so on, the amplitude first increases, and then decreases with the increasing size, one after another.

Figure 2.4 Extinction spectrums calculated with the Mie theory for spheres of (a) Al, (b) Na, (c) Ag and (d) Au. In figure legends, 2R stands for diameter of a nanosphere. Optical constants are taken from reference.³²

Taking Na's spectrum as an example, when the size is 30 nm in diameter, the peak around 390 nm is due to dipole mode, and it is very close to the size-independent peak wavelength of 384 nm obtained by equation (2.2) (or as in Figure 2.3 (a)). Then, when the diameter increases to 60 nm, the dipole peak is red-shifted to around 420 nm, and a quadruple peak weakly occurs around 350 nm. When the diameter is increased to 90 nm, both peaks shift to longer wavelength, and the quadruple peak's amplitude increases and can now be clearly recognized, while the amplitude of dipole peak start to decrease. When the diameter increases to 120 nm, this trend continues, i.e. both dipole and quadruple peaks red-shift, with dipole peak's amplitude decrease and

quadruple peak's amplitude increase. And when the diameter is increased to 150 nm, an octupole peak can be recognized around the wavelength of 350 nm. Although not depicted in those graphs, this trend keeps going on, i.e. each mode's peak appear, red-shifts, increases then fades, one after another.

C. Effect of refractive index of surrounding medium

The effect of increasing the refractive index of surrounding medium red-shifts the extinction peak, without too much change on the shape of those peaks, except for a broadening of peaks. This trend is depicted in Figure 2.5 shown below.

Figure 2.5 Extinction spectrum calculated by Mie's theory for (a) Na in vacuum (refractive index of medium $n=1$), and (b) Na in water (refractive index of medium $n=1.33$). In figure legends, 2R stands for diameter of a nanosphere. Optical constants of Na are from reference.³²

The obvious redshift by about 120 nm by changing the medium's refractive from 1 to 1.33 can be comprehended in the following way. The surrounding dielectric decreases the surface charge, because of partial compensation by the polarization of the medium. The decreased surface charge corresponds to a smaller restoring force which in turn shifts the resonance frequency to lower values, i.e. a red shift. It is similar to the case of a oscillating spring, if the restoring force of a spring is decreased, assuming the damping does not change, then the resonant oscillation of the spring is decreased.

D. Effect of particle's shape

For non-spherical metallic nanoparticles, the surface plasmons are affected by the non-uniform surface curvature, for example edges, corners. For arbitrary shapes of nanoparticle, numerical methods are employed, such as discrete dipole approximation (DDA) and T-matrix method.³³⁻³⁴ In general, multi-peaks occur due to the non-uniform surface curvature. Examples include ellipsoids, cubes, rods, triangular plates.^{17, 25, 35-41} In this section, they are briefly reviewed, and for simplicity, spectrum examples are only shown for nanorod and triangular plate.

Figure 2.6 (a) The extinction spectrum measured for gold nanorods, taken from reference,⁴² inset shows TEM image of the gold nanorods, (b) Efficiencies spectrum for an equilateral triangular nanoplate with 100 nm in side length, and 16 nm in thickness, calculated by discrete dipole approximation (DDA), taken from reference.⁴¹

For an arbitrary ellipsoid, three resonances exist for a sample where many of this ellipsoid are randomly oriented, and these three resonances are attributed to electrons oscillating along the three major axes,^{16, 25} The optical properties of nanocube were investigated by Napper and Fuchs.⁴³⁻⁴⁴ Distinct resonances corresponding to special modes due to edge and corner are observed. For metallic nanorods, there are two resonances, one located at a longer wavelength (low frequency), and the other located at a short wavelength (high frequency). The high frequency mode corresponds to electrons oscillating perpendicularly to the major axis; whereas the low frequency mode

results from electron oscillation along the major axis (Figure 2.6 (a)). In the case of triangular nanoplates, two kinds of resonances are generally identified, one group of resonances belong to bulk plasmon modes, the other is due to the large localized enhancement at their sharp tips (Figure 2.6(b)).

E. Effect of coating shell

Nanoparticles can be made up of more than one metals to form core-shell or alloys structures. Alloy sphere can be treated as one uniform sphere, with its dielectric functions given by effective medium approximation.⁴⁵⁻⁴⁷ For core-shell structure, it may consist of many concentric layers surrounding the core. As additional internal boundary conditions must be satisfied, special plasmon resonance modes can be excited, in the core and in the shells, leading to complicated extinction spectra.⁴⁸⁻⁴⁹ Since the most easily achieved core-shell structure is that of only one shell, only the features of the one-shell core-shell structure is discussed here. For a general multi-shell structure (number of shells ≥ 1), a recursive algorithm is reviewed in Section 3.1

Figure 2.7 Measured extinction spectrums of silver shelled gold (a), with core diameter of 12 nm, and various thicknesses of 0, 0.5, 0.9, 1.1, 2.2, 6.5 nm from bottom up; and of gold shelled silver (b), with core diameter of 27.2 nm, and shell thicknesses of 0, 2.2, 3.0, 4.6, 7.2, 9.0 nm from bottom up. Figure is taken from reference.⁵⁰

Figure 2.7 shows measured and calculated extinction spectra of an Au core coated with Ag shell (a), and an Ag core coated with Au shell (b).⁵⁰ The extinction spectrums

gradually change from that of nanoparticle purely composed of core material to that of nanoparticle purely composed of shell material, as the shell thickness increases. But the intermediate spectrums are quite different from either of the pure nanoparticle's spectrums.

Figure 2.8 Calculated extinction spectrums for core-shell structure, (a) dielectric ($n=3.16$) as core, with core diameter of 4 nm, and Na as shell, thickness increasing from 0.2 nm (front) to 18 nm (back); (b) Na as core, dielectric as shell, thicknesses are the same as in (a). Figure is taken from reference.¹⁶

For the combination of dielectric material and metallic material, in Figure 2.8 a calculated example is given for Na and a surrounding medium with a fictitious refractive index 3.16, with (a) dielectric as core and Na as shell., and (b) the other way around.¹⁶ It is observed that the covering of a Na core with dielectric shell leads to a red shift of the extinction peak. This can also be understood in the same way of the effect of increasing surrounding medium refractive index: the dielectric shell decreases the surface charge, due to partial compensation by the polarization of the shell. The decreased surface charge corresponds to a smaller restoring force which in turn shifts the resonance frequency to lower values. If the shell thickness is very thick, the extinction resonance converges to the case where Na is embedded in a surrounding medium of 3.6. While in the reverse case, i.e. dielectric material as core and Na as shell, a resonance splitting is observed. The two observed resonance peaks are related to the sodium shell's two interface, one with the vacuum, the other one with the dielectric.

2.2 Applications of metallic nanoparticle's LSPR

In this section, a few examples are given to show applications of metallic nanoparticle's LSPR in bio-sensing,⁵¹⁻⁵² surface enhanced raman scattering (SERS),¹⁷ and transparent projection display.¹³⁻¹⁵ Since this thesis' focus is on transparent projection display based on metallic nanoparticle's LSPR, the first two applications (bio-sensing and SERS) are briefly discussed, while 3 existing solutions for the third one (transparent projection display based on metallic nanoparticle's LSPR) are reviewed in detail.

In photoacoustic imaging as described in reference,⁵¹ target cells or organs are illuminated by laser pulses. The wave length of the incident light is usually from 800 nm to 1300 nm, a region of high physiological transmissivity which has been shown as the best region suitable for applications of optical bioimaging and bio-sensing.⁵² The incident light is then absorbed and transformed into outgoing thermoacoustic wave that can be captured and used to reconstruct images. Since the target cells or organs may not be efficient in absorbing the light and converting it into heat, the images constructed do not possess good contrast ratio. Thus, contrast agents that have high absorption cross section are attached to these cells or organs to increase the contrast ratio of constructed image. Due to gold nanoparticles' superior optical properties, biocompatibility, and ease of bioconjugation, gold nanorods, nanocages, and nano-shells have been used as contrast agents for photoacoustic imaging.⁵³⁻⁵⁴ And in reference,⁵² gold nano-shells are designed as biological labels based on high scattering cross section, and as photothermal therapy of tumours based on high absorption cross section.

The SERS is also based on the LSPR effect. When a metal nanoparticle is in resonance, the near fields is enhanced. And this enhanced near field can increase Raman scattering intensities of the investigated molecules if they are deposited on surfaces of metal nanoparticles. SERS is shown to be very strong, achieving four orders of magnitude if metal nanoparticles were used as substrates for the Raman active molecules.⁵⁵⁻⁵⁶

As for application of metallic nanoparticle's LSPR in transparent projection display, Figure 1.1 shows the ideal case. Therefore, this method relies on the design of optical resonant scatterers that are strongly frequency-selective and have low absorption. Thus, metals are chosen by first checking whether they have the potential to generate sharp resonant peak(s) (i.e., strong frequency-selectivity). As discussed in part A of Section 2.1, two approaches, which correspond to equation (2.3) and equation (2.4), can be used to determine sharpness of resonant peak. And both equation (2.3) and equation (2.4) lead to the same conclusion: around interested wavelengths (i.e., wavelengths for red, green and blue light in this case), for the resonant peak to be sharp, the dielectric function of a qualified metal should have a small imaginary part or a real part with fast changing rate with respect to wavelength (or frequency). So, it is useful to plot $\eta = \left| \frac{d\varepsilon_1}{d\lambda} / \varepsilon_2 \right|^2$ in visible spectrum range (400 nm ~ 800 nm) for different metals, which is shown in Figure 2.9, and choose the appropriate ones from the plotting. By observing Figure 2.9, it is obvious that Silver (Ag) has the largest value for most part of the visible spectrum, while Gold (Au) has the largest value around the wavelength of 700 nm. Therefore, Ag is the most suitable candidate for the whole visible spectrum, while Au may be suitable around red light. And for this reason, the three types of nanostructures to be reviewed in the following all work with Ag.

Figure 2.9 An initial estimator of performance for small metallic nanoparticle's wavelength selectivity. Definition of η is given in text. Figure is taken from reference.¹³

In the following parts (A, B and C), selective scattering of spherical core-shell nanoparticle Silica@Ag (core@shell) is first reviewed,¹³ followed by that of ellipsoidal nanoparticles,¹⁵ and finally that of metallic nanocubes.¹⁴

A. Selective scattering by spherical core-shell nanoparticle Silica@Ag (core@shell)

Sphere-shaped nanoparticle is highly symmetric, and therefore does not need alignment when dispersed in a transparent matrix. Ag's resonance peak wavelength under quasi-static approximation (i.e., particle size $\ll$ wavelength) is about 416 nm when surrounding environment has a refractive index of 1.5 (dielectric function ϵ_m of this surrounding medium is a constant given by the square of its refractive index), according to the resonance condition given by equation (2.2) ($\epsilon_1(\omega) = -2\epsilon_m$). Note, refractive indexes of most polymers and glasses are around 1.5, and at the end of the day, nanoparticles engineered for transparent projection display are to be dispersed in polymer or glass. However, the wavelength ranges for blue, green and red light are 450 nm to 490 nm, 520 nm to 560 nm and 635 nm to 700 nm, respectively.⁵⁷ Thus, it is necessary to red-shift Ag's resonance peak wavelength under quasi-static limit into the three wavelength regions of red, green and blue light. And one approach is by the core-shell structure with Silica as core and silver as shell (Silica@Ag).¹³

For the purpose of tuning structural parameters (core diameter, and shell thickness) to achieve an optimal trade-off between light scattering frequency-selectivity and light absorption level, it is necessary to quantize the desired performance by a mathematical expression. To achieve this, the following Figure of Merit (*FOM*) is defined:

$$FOM = \frac{\sigma_{sca}(\lambda_0)}{2\overline{\sigma_{sca}} + \max\{\sigma_{abs}\}} \quad (2.6)$$

where λ_0 is the resonant wavelength, the overline and the symbol $\max\{\dots\}$ respectively denote the mean and the maximum in the visible spectrum (from 400 nm to 800 nm), σ_{sca} and σ_{abs} are the scattering and absorption cross sections of a nanoparticle respectively, which can be calculated by either Mie theory or transfer matrix method.^{30, 49, 58} By observing equation (2.6), it is obvious that a high value of

FOM favours the following properties: low absorption cross-section over the whole visible spectrum, a high scattering cross-section at the resonance wavelength, and low scattering cross-section elsewhere, i.e. a narrow or sharp resonance peak. Therefore, the *FOM* defined in equation (2.6) captures the desired performances: scatterers should be strongly frequency-selective and have low absorption. This *FOM* is also used in next Section “*Selective scattering by Ag ellipsoids*”, as well as in Chapter 4 and Chapter 6.

Optimization of *FOM* is through the algorithm of multi-level single-linkage,⁵⁹ which can be implemented in the free package of nonlinear optimization NLOpt.⁶⁰ They have assumed that the transparent matrix (Polyvinyl Alcohol, or PVA in short) in which nanoparticles of Silica@Ag are embedded has a refractive index of 1.44. Refractive index for Silica is assumed to be 1.45 and dielectric constants for Ag is from reference.³² However, it should be pointed out that direct usage of Ag’s dielectric constants from reference is not appropriate, as this omits effect of surface dispersion of conduction electrons which increases light absorption and decreases light scattering,⁶¹⁻⁶² and this effect is numerically demonstrated later in Chapter 5.

Optimized results from Silica/Ag are shown in Figure 2.10 as well as Table 2.1.

Figure 2.10 Calculated cross-sections of scattering and absorption for Silica@Ag (core@shell) nanoparticles (embedding medium has a refractive index of 1.44). And optimizations are performed for them to scatter monochromatic light at (a, blue) $\lambda_0=458\text{nm}$, (b, green) 532nm , and (c, red) 640nm . Relative sizes of the structures are shown by insets; r denotes the outer radius of the particle. Figure is taken from reference.¹³

Table 2.1 Optimized size parameters of particle and FOM for spherical core-shell structure of Silica@Ag. Table is adapted from reference.¹³

Wavelength λ_0	Core radius	Shell thickness	FOM
458 nm	1.3 nm	30.8 nm	1.01
532 nm	22.2 nm	15.8 nm	0.91
640 nm	34.3 nm	11.0 nm	0.81

Due to difficulty in precise synthesis of Silica/Ag structure,⁶³ experimental verification was conducted only for blue-color-only transparent projection display with spherical Ag nanoparticles with average diameter of 62 nm (Silica core with radius of 1.3 nm is omitted). A blue-color-only transparent projection display was made by embedding spherical Ag nanoparticles with average diameter of 62 nm into PVA polymer-matrix. This film has a thickness of 0.46 mm, and the areal concentration of Ag nanoparticles is about $6 \times 10^9/cm^2$, or an equivalent mass concentration of $7\mu g/cm^2$. As shown in Figure 2.11 (a) and (b), measured transmittance and extinction spectrum agrees well with results from simulation. Simulated results of light scattering and absorption in Figure 2.11 (b) indicates scattering around resonance wavelength is significantly stronger than the absorption around resonance wavelength, which may not remain true if effect of surface dispersion of conduction electrons is included. Angular distribution of scattered light shown in Figure 2.11 (c) indicates that the scattering is very isotropic and polarization-independent. And these suggest the scattered light from the display can be viewed from a wide angle and the display can be operated with incident light with arbitrary polarization.

Figure 2.11 Characterization of the transparent projection film made by dispersing Ag nanospheres with average diameter of 62 nm in PVA. (a) Comparison of the measured and theoretically calculated transmittance spectrums; width of the experimentally measured curve stands for one standard deviation over different wavelength of incident light. Inset is a TEM image of the Ag nanospheres with average diameter of 62 ± 4 nm. Scale bar of the TEM image is 200 nm. (b) Comparison of extinction spectrums from experimental measurement and theoretical calculation, theoretically calculated scattering and absorption are also shown. (c) Angular distribution of light scattering at the wavelength of 458 nm, with electric field of the normally incident light polarized parallel (p) and perpendicular (s) to the scattering plane. Figure is taken from reference.¹³

In Figure 2.12, the transparent projection display at work is shown. The projected image shows up clearly on the display embedded with Ag nanoparticles. As a comparison, the same projected image on the usual glass (the right one) can hardly be observed because of little scattering.

Figure 2.12 The transparent projection display in work (left) compared with a normal piece of glass (right). A blue MIT icon is projected onto both the transparent projection display and the normal glass by a laser projector (MicroVision SHOWWX+, wavelength of blue light is 458 ± 2 nm); the image can be clearly viewed on the transparent projection display, while not on the normal glass. They place three cups with RGB letters behind the film to intuitively demonstrates the transparency. Figure is taken from reference.¹³

B. Selective scattering by Ag ellipsoids

Apart from the structure of Silica@Ag, the shape of ellipsoid provides another alternative for tuning of resonant wavelength λ_0 .

The geometry array under consideration is illustrated in Figure 2.13, which consists of a periodic 2-dimensional array of Ag ellipsoids settled in a square lattice and surrounded by a transparent dielectric environment with dielectric constant of ϵ_h ($=2.1$, or an equivalent refractive index of 1.45). The distance between two adjacent Ag ellipsoids' geometric centres is denoted with d , and is equal to 100 nm. The major semi-axis along y-axis is denoted as a , and the two minor semi-axes b, c are assumed to be equal. The propagation direction of the incident light is assumed to be normal to the plane of the periodic array, and electric field oscillation of incident light is along the major semi-axis (i.e., a TE-plane wave).

Figure 2.13 The proposed geometry array of Ag ellipsoids: ellipsoids are placed in a square lattice and the incident light has its electric field aligned along the major axis of the ellipsoids (i.e., TE-plane wave illumination). d is the distance among centres of two adjacent nanoparticles, while a , b , and c are the major and minor axes of the ellipsoids, respectively. Figure is taken from reference.¹⁵

Instead of simply taking Ag's dielectric constants from reference, as done in the case of Silica@Ag, in this work, Ag's dielectric constants have been modified to take into account effect of surface scattering of conduction electrons since the Ag ellipsoids' sizes are comparable to electron's mean free path in bulk silver, which is about 52 nm.⁶² The details of how to modify Ag's dielectric constants to consider effect of surface scattering of conduction electrons will be explained in Chapter 4 and Chapter 5, and will be omitted here to avoid unnecessary confusion.

Through an analytical model,⁶⁵⁻⁶⁸ it is concluded that resonance peak wavelength of a Ag ellipsoid is mainly affected by eccentricity, and that a trade-off between sharpness of scattering peak (i.e., frequency-selectivity of scattering) and light absorption level cannot be avoided when adjusting its size. And it is found the eccentricity is equal to 0.96, 0.9, and 0.81 for the arrays responsible for scattering of red, green and blue light, respectively. Therefore, as a first estimation, it is useful to fix eccentricity of a set of Ag ellipsoids to 0.96, 0.9 or 0.81 and tune their major axis a to maximize FOM defined by Equation (2.6). The result of this initial maximization is shown in Figure

2.14.

Figure 2.14 Initial optimization of Ag ellipsoids for selective scattering of the three basic additive colours (red, green and blue). For each basic array of Ag ellipsoids, the nanoparticles' major axis has been swept from 20 nm to 40 nm while their eccentricity is fixed to 0.96, 0.9, and 0.81 for the arrays responsible of red, green and blue light, respectively. As a comparison, values of the *FOM* without consideration of effect of surface scattering of conduction electrons are also shown (dashed lines). Figure is taken from reference.¹⁵

In Figure 2.14, *FOM* calculated without considering surface scattering of free electrons (i.e., directly use Ag's dielectric constants from reference) are also shown as dashed lines. It is clear that at smaller sizes, values of *FOM* calculated without surface scattering are much larger than those calculated with surface scattering. As will be shown later in Chapter 5, without consideration of surface scattering of free electrons, scattering level is overestimated, absorption level is underestimated and peak width is narrower (i.e., frequency-selectivity of light scattering is overestimated).

Starting from the initially optimized results from Figure 2.14, the final optimized Ag ellipsoids for red, green and blue light selective scattering are shown in Table 2.2.

Table 2.2 Optimal particle sizes and FOM for ellipsoidal Ag nanoparticles.

Wavelength λ_0	a	b	FOM
461 nm	25 nm	17 nm	0.93
530 nm	26 nm	13 nm	1.1
678 nm	30 nm	9 nm	1.6

Since the optimized ellipsoidal Ag nanoparticles in Table 2.2 are obtained by assuming incident light to be TE-plane wave, the design shown in Figure 2.15 is proposed to realize a full-colour and almost-isotropic transparent projection display.

Figure 2.15 Proposed unit-cell of the transparent projection display that is full-colour and almost polarization-independent achieved with Ag ellipsoid arrays. The propagation direction of the incident light is along the negative direction of the z-axis. This unit-cell repeats itself in the x-y plane along the x- and the y-axes with period $d = 100$ nm. Each unit cell consists of two replicas of each of the optimized nanoparticle array in Table 2.2, and one set is rotated by 90° to the other, with adjacent layers separated by a distance t . To ensure coupling between two adjacent layers is negligible, a minimum value of t is confirmed to be 100 nm by simulations. Figure is taken from reference.¹⁵

The full-wave results of the proposed structure depicted by Figure 2.15 are shown in Figure 2.16, where results for both polarizations of incident light (i.e., oscillating electric field along x- and y-axes) are plotted.

Figure 2.16 Scattering (SCS) and absorption (ACS) cross sections calculated for the display proposed in Figure 2.15 under incident light separately of each polarization (TE and TM). Figure is taken from reference.¹⁵

As observed from Figure 2.16, the three scattering peaks are reasonably sharp, and the overall absorption level is reasonably low. Average transmittance calculated for the TE polarization incidence is 52%. The small differences between results of two incident polarizations are due to residual coupling among different layers. The 3D scattering patterns for the TE incident polarization of the optimized Ag ellipsoids in Table 2.2 are shown in Figure 2.17, which indicate the scattering patterns are almost isotropic.

Figure 2.17 3D angular scattering distribution for the optimized Ag ellipsoids in Table 2.2: (left) Ag ellipsoid array for selective red light scattering, (center) Ag ellipsoid array for selective green light scattering and (right) Ag ellipsoid array for selective blue light scattering. Scale is the same for all subfigures. Figure is taken from reference.¹⁵

Finally, it has been shown through simulations that when half of the ellipsoids in the design depicted by Figure 2.15 are randomly shifted up to 15 nm in the xy-plane, the performance is not affected. Also, for the design in Figure 2.15, it is shown that variation of eccentricity does not have significant effect on performance up to a minor axis change ratio of 2.5%. Thus, it is believed the design in Figure 2.15 has some robustness towards geometrical imperfections.

C. Selective scattering by Ag Nanocubes

Ag nanocube may provide another alternative for selective scattering.^{14, 38} As shown in Figure 2.18, when a Ag nanocube is put on a dielectric substrate, its single LSPR light scattering peak splits into two: the distal mode (peak 1) and the proximal mode (peak 2). And it has been shown the higher the refractive index of the substrate, the larger the distance between the two peaks.⁶⁹ As will be shown later, when TiO₂ which has high refractive index is chosen as the substrate, the peak at lower wavelength is suitable for selective backscattering of blue light.

Figure 2.18 FDTD (finite-difference time-domain) simulations showing (A) a second peak emerges when a single Ag nanocube (edge length of 90 nm) approaches a glass substrate (index assumed to be 1.5), and the near field $|E|$ plots for (B) peak 1 and (C) peak 2 of the nanocube placed on the glass substrate. The surrounding medium is air, and the white line in (B), (C) represent the interface between Ag nanocube (or Air) and the glass substrate. Figure is taken from reference.⁶⁹

As shown in Section 2.1, both peak wavelength and intensity of scattering spectrum are affected by nanoparticle's size, so in Figure 2.19, backscattering spectrums are first calculated for Ag nanocubes of 3 sizes (edge lengths of 80 nm, 100 nm and 120 nm) on

sufficiently thick TiO_2 (800 nm) to gain an insight of an optimal size.

Figure 2.19 Simulated backward scattering spectrums with FDTD for Ag nanocubes deposited on TiO_2 with sufficient thickness (800 nm). The luminosity function is also shown to indicate that human eyes are not sensitive to blue and red light. TiO_2 's refractive index is from reference.⁷⁰ Ag's refractive index is from reference.³² Figure is taken from reference.¹⁴

It is concluded that Ag nanocube having an edge length of 100 nm is more suited for projection display for two reasons: 1. The two peak wavelengths of its scattering peaks are around 440 nm and 640 nm wavelength regions, respectively, which are more suitable for blue and red light scattering; 2. It is more difficult to synthesize nanocube of larger sizes. In this section, it is believed that enhancement of green light backscattering is not important since human eyes are sensitive to green light (see the photopic luminous curve in Figure 2.19). As observed from Figure 2.19, backscattering of red light is much weaker compared to that of blue light, so it is desirable to enhance backscattering of red light. If more red light is reflected at the air/ TiO_2 interface, then more red light is expected to be scattered by Ag nanocube, and hence backscattering of red light is expected to be enhanced. Reflection of red light can be increased by making use of constructive optical interference: make the red light reflected at the air/ TiO_2 interface constructively interfere with that reflected at the TiO_2 /glass interface (the substrate is assumed to be glass). Since the light intensity experienced by the Ag nanocube may sometimes be disturbed by the presence of the nanocube itself, the backscattering cross sections of the Ag nanocube (100 nm of edge length) on TiO_2 films of different thicknesses have been calculated and plotted in Figure 2.20 to seek out the

appropriate TiO₂ thickness.

Figure 2.20 Simulated results to show TiO₂ thickness versus the blue light and red light backward scattering cross sections at peak wavelength of a Ag nanocube with edge length of 100 nm on TiO₂. Figure is taken from reference.¹⁴

And from Figure 2.20, it is concluded that a thickness of 110 nm for TiO₂ film is the most suitable, since at this film thickness, backscattering of red light is the strongest and backscattering of blue light is reasonably high.

Following theoretical considerations, experimental verification was conducted. TiO₂ thin film with a thickness of 110 nm was deposited on one side of a piece of 320rosilicate glass slip. Then, Ag nanocubes with average edge length of 100 nm was synthesized and deposited on the TiO₂ thin film (areal density is around 3.5×10^8 particles per cm²) by casting an ethanolic dispersion of the nanocubes followed by evaporation of ethanol and a rinse with deionized water. For this experimentally prepared transparent projection display, its measured backscattering spectrum is shown in Figure 2.21(a), and its transmittance spectrum is shown in Figure 2.21(b).

Figure 2.21 (a) spectrum of backward scattering and (b) transmittance spectrum of the transparent projection display experimentally fabricated by depositing a monolayer of Ag nanocubes (edge lengths have an average value of 100 nm) on the film of TiO_2 with thickness of 110 nm. The TiO_2 film is deposited on glass substrate. The luminosity function is also shown in (a). Figure is taken from reference.¹⁴

Figure 2.22 shows the display at work (left) and its transparency where no image is projected (right).

Figure 2.22 (left) A colourful image is projected onto the experimentally prepared transparent projection display, model of the projector is Epson EB-1761W, whose peak wavelengths of blue, green, and red light are at 442, 552, and 612 nm, respectively; (right) Transparency of the experimentally prepared transparent display when no image is projected. Figure is taken from reference.¹⁴

As observed from Figure 2.21 and Figure 2.22, colourful images can be displayed on this transparent projection display, and it is colourless and transparent where no image is projected.

Chapter 3. Methodology

In this chapter, methods for simulating nanoparticle's light scattering and absorption, and method of measuring material's dielectric function are reviewed.

3.1 Methods for simulating nanoparticle's light scattering and absorption

Before reviewing the modelling methods for simulating nanoparticle's light scattering and absorption, it is useful to have an intuitive idea of what are light scattering, absorption and extinction.

When parallel rays of incident light encounter an obstacle during their propagation, some of them get deflected from their original propagation direction through mechanisms such as reflection or refraction, some of them are absorbed, as shown in Figure 3.1.³⁰ The rays of light that are deflected from their original propagation direction are said to be scattered. And the extinction is simply the addition of the scattering and absorption (i.e., the amount of light not propagating along the original incident direction).

Figure 3.1 Light scattering and absorption by an arbitrary particle. Figure is taken from reference.³⁰

Macroscopically, incident light rays will interact with an obstacle only when their propagation paths are geometrically blocked by this object. Imagining a paper whose surface is normal to the incident light rays placed behind the obstacle, the rays blocked by the obstacle will generate a shade on this paper, and the area of this shade is the geometric as well as the extinction cross section of this macroscopic obstacle.

However, for obstacles whose sizes are of the order less than 1000 nm, light rays will be affected by the obstacle even if their lines of propagation are near (not necessarily blocked by) the obstacle. Thus, the extinction cross section is generally not equal to the geometric cross section. Quantitatively, the cross sections are calculated by the ratio of corresponding power losing rates (i.e. extinction, scattering and absorption) to the intensity of the parallel incident light. Since power losing rate has the unit of Joule/Sec, and intensity of incident light has the unit of Joule/(Sec·m²), the extinction, scattering and absorption cross sections, which are denoted as σ_{ext} , σ_{sca} and σ_{abs} , respectively, have the unit of area: m² (or nm² as mostly used).

Sometimes, for ease of comparison, these cross sections are normalized by the obstacle's geometrical cross section, taking sphere as an example:

$$Q_{sca} = \frac{\sigma_{sca}}{\pi r^2}$$
$$Q_{abs} = \frac{\sigma_{abs}}{\pi r^2}$$
$$Q_{ext} = \frac{\sigma_{ext}}{\pi r^2}$$

where r is the radius of the sphere. Q_{sca} , Q_{abs} and Q_{ext} are the scattering, absorption and extinction efficiencies respectively.

The simplest case of scattering and absorption is that of a single homogeneous sphere. And the problem is well handled by the Mie theory, which gives the simple, exact analytical solution to Maxwell's equations.³⁰ Besides the single sphere, Mie theory also has some extensions to coated spheres,⁵⁸ infinite cylinders,⁷¹⁻⁷² and spheroids.⁷³

However, since particles of interest do not necessarily have to be shapes that can be solved by Mie's extensions, there is a need for numerical based methods for simulating arbitrarily-shaped particles. Numerical models include Discrete Dipole Approximation (DDA),^{33, 74} Finite Difference Time Domain (FDTD),⁷⁵⁻⁷⁶ and T-Matrix method,^{34, 77} each having their particular suitable scenarios of applications, and are reviewed in references.⁷⁸⁻⁷⁹

In the subsequent chapters, the Mie theory and its extension to coated sphere are used for simulations of spherical nanoparticles, and FDTD is employed for simulations of cube-shaped nanoparticles. Therefore, in the following two subsections, physical and mathematical principles of these two simulation methods are briefly reviewed.

3.1.1 The Mie theory

In a simple way, the Mie theory is a black box. And for this black box, its inputs are the surrounding medium's refractive index, the nanoparticle's constituent materials' refractive indexes, and the nanoparticle's geometrical dimensions (e.g., for a spherical core-shell structure, core diameter and shell thickness are the geometrical dimensions). And the outputs of this black box are the extinction, scattering and absorption cross sections (or efficiencies). The Mie theory decomposes the total extinction spectra into dipolar, quadrupolar and higher modes of electronic excitations and sum them up. With 1st order being the dipole mode, 2nd order being the quadrupole mode, 3rd order being the octupole mode and so on. Each multipole contributes by electric and magnetic modes, i.e. plasmons and eddy currents which each consist of absorption and scattering losses, as shown in Figure 3.2.¹⁶ And the summation of scattering (absorption) contributions from all modes (dipolar, quadrupolar and so on) gives total scattering (absorption) cross section of a nanoparticle.

Figure 3.2 Decomposition of the total extinction spectra in dipole, quadrupole and higher modes of electronic excitations. Figure is taken from reference.¹⁶

The mathematical procedures of the Mie theory to calculate scattering, absorption and extinction cross sections for a single homogeneous sphere are separated into 3 stages as summarized from chapters 4, 5 and 7 of reference,³⁰ and are shown in the Figure 3.3.

Figure 3.3 Three stages of the Mie theory's mathematical procedures to calculate scattering, absorption and extinction cross sections for a single homogeneous sphere.

The three stages are explained in detail below.

Stage 1: express waves in a series of vector spherical harmonics

Expressing incident, scattered and interior waves into vector spherical harmonics is for the sake of making use of the boundary conditions of the electric and magnetic fields at the sphere surface.

Figure 3.4 Schematic illustration of the coordinate setup of light scattering by a nanosphere. Figure is taken from reference.³⁰

With the choice of a spherical coordinates, which is shown in Figure 3.4, a set of linear independent and orthogonal vector spherical harmonics $M_{e_{nm}}$ and $N_{e_{nm}}$ are created and are given by:

$$M_{e_{nm}} = \begin{pmatrix} 0 \\ -\sin(m\varphi) \frac{mP_{nm}(\cos\theta)}{\sin\theta} z_n(\rho) \\ -\cos(m\varphi) \frac{dP_{nm}(\cos\theta)}{d\theta} z_n(\rho) \end{pmatrix} \quad (3.1)$$

$$M_{o_{nm}} = \begin{pmatrix} 0 \\ \cos(m\varphi) \frac{mP_{nm}(\cos\theta)}{\sin\theta} z_n(\rho) \\ -\sin(m\varphi) \frac{dP_{nm}(\cos\theta)}{d\theta} z_n(\rho) \end{pmatrix} \quad (3.2)$$

$$N_{e_{nm}} = \begin{pmatrix} \cos(m\varphi) \cdot n(n+1) \cdot P_{nm}(\cos\theta) \frac{z_n(\rho)}{\rho} \\ \cos(m\varphi) \frac{dP_{nm}(\cos\theta)}{d\theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \\ -\sin(m\varphi) \frac{mP_{nm}(\cos\theta)}{\sin\theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \end{pmatrix} \quad (3.3)$$

$$N_{onm} = \begin{pmatrix} \sin(m\varphi) \cdot n(n+1) \cdot P_{nm}(\cos\theta) \frac{z_n(\rho)}{\rho} \\ \sin(m\varphi) \frac{dP_{nm}(\cos\theta)}{d\theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \\ \cos(m\varphi) \frac{mP_{nm}(\cos\theta)}{\sin\theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \end{pmatrix} \quad (3.4)$$

With the abbreviation $\rho = kr$, $k = (2\pi n)/\lambda$ being the wave number in the embedding medium. The symmetry of the sphere allows m to be set to 1. The quantity z_n is one of the four spherical Bessel functions: spherical Bessel functions j_n , or spherical Neumann functions y_n , or spherical Hankel functions of the first kind $h_n^{(1)}$, or of the second kind $h_n^{(2)}$. $P_{nm}(\cos\theta)$ is the associated Legendre polynomial.

It is assumed that the particle is surrounded by a non-absorbing medium with refractive index n_M . And the size parameter in the surrounding medium is defined as $x = k_M R$, with $k_M = (2\pi n_M)/\lambda$; and in the particle $n_P/n_M x = k_1 R$, with $k_1 = (2\pi n_P)/\lambda$. With the above defined vector harmonics, the electromagnetic fields for a plane wave propagating along the z-axis, being polarized parallel the x-axis are as follows:

Incident wave:

$$E_{inc} = E_0 \sum_{n=1}^{\infty} \frac{i^n (2n+1)}{n(n+1)} [M_{on1}^{(1)}(k_M) - iN_{en1}^{(1)}(k_M)] \quad (3.5a)$$

$$H_{inc} = \frac{-k_M E_0}{\omega \mu_0} \sum_{n=1}^{\infty} \frac{i^n (2n+1)}{n(n+1)} [M_{en1}^{(1)}(k_M) + iN_{on1}^{(1)}(k_M)] \quad (3.5b)$$

Scattered wave:

$$E_{sca} = -E_0 \sum_{n=1}^{\infty} \frac{i^n (2n+1)}{n(n+1)} [b_n M_{on1}^{(3)}(k_M) - i a_n N_{en1}^{(3)}(k_M)] \quad (3.6a)$$

$$H_{sca} = \frac{k_M E_0}{\omega \mu_0} \sum_{n=1}^{\infty} \frac{i^n (2n+1)}{n(n+1)} [a_n M_{en1}^{(3)}(k_M) + i b_n N_{on1}^{(3)}(k_M)] \quad (3.6b)$$

Wave inside the particle:

$$E_1 = E_0 \sum_{n=1}^{\infty} \frac{i^n(2n+1)}{n(n+1)} \left[\beta_n^1 M_{on1}^{(1)}(k_1) - i\alpha_n^1 N_{en1}^{(1)}(k_1) \right] \quad (3.7a)$$

$$H_1 = \frac{-k_1 E_0}{\omega \mu_0} \sum_{n=1}^{\infty} \frac{i^n(2n+1)}{n(n+1)} \left[\alpha_n^1 M_{en1}^{(1)}(k_1) + i\beta_n^1 N_{on1}^{(1)}(k_1) \right] \quad (3.7b)$$

In equations (3.6) and (3.7), a_n , b_n are the unknown expansion coefficients for scattered wave, and α_n , β_n are the unknown expansion coefficients for waves inside the particle. The superscript of the vector harmonics indicates the kind of spherical function represented by z_n : '1' stands for spherical Bessel functions j_n , '3' stands for the spherical Hankel functions of the first kind $h_n^{(1)}$.

Stage 2: apply Maxwell's boundary conditions to solve for expansion coefficients

In this stage, Maxwell's boundary conditions at the surface of the particle are applied:

$$(E_{inc} + E_{sca}) \times e_r|_{r=R} = E_1 \times e_r|_{r=R} \quad (3.8)$$

$$(H_{inc} + H_{sca}) \times e_r|_{r=R} = H_1 \times e_r|_{r=R} \quad (3.9)$$

In equations (3.8) and (3.9), e_r is a unit vector radiating from the origin to the point on the surface of the particle. Equations (3.5) (3.6) (3.7) are substituted into equations (3.8) and (3.9) to solve for the unknown expansion coefficients a_n , b_n and α_n , β_n . Since only the wave scattered (far field) is interested in this thesis, only a_n , b_n are shown here:

$$a_n = \frac{\psi_n(x)\psi_n'(mx) - m\psi_n'(x)\psi_n(mx)}{\xi_n(x)\psi_n'(mx) - m\xi_n'(x)\psi_n(mx)} \quad (3.10)$$

$$b_n = \frac{m\psi_n(x)\psi_n'(mx) - \psi_n'(x)\psi_n(mx)}{m\xi_n(x)\psi_n'(mx) - \xi_n'(x)\psi_n(mx)} \quad (3.11)$$

In equations (3.10) and (3.11), $m = n_p/n_M$ stands for the relative refractive index of the particle. $\psi_n(x) = xj_n(x)$, $\xi_n(x) = xh_n^{(1)}(x)$ are the Riccati-Bessel, Riccati-Hankel functions respectively. The prime denotes derivation with respect to its argument.

Stage 3: obtain cross sections

The extinction and scattering rates are obtained through surface integration of the

Poynting vector outside the particle. For a particle with radius R , it is convenient to use the surface of a conceptual concentric sphere with radius $R_{cs} \geq R$ to conduct the surface integration. The rates are given below:

$$W_{ext} = -\frac{1}{2} Re \int_0^{2\pi} \int_0^\pi (E_{inc} \times H_{sca}^* + E_{sca} \times H_{inc}^*) e_r R_{cs}^2 \sin\theta d\theta d\varphi \quad (3.12)$$

$$W_{sca} = -\frac{1}{2} Re \int_0^{2\pi} \int_0^\pi (E_{sca} \times H_{sca}^*) e_r R_{cs}^2 \sin\theta d\theta d\varphi \quad (3.13)$$

Extinction and scattering cross sections can be obtained by dividing equation (3.12) and (3.13) by the intensity I_0 of the incident light. The manipulations are omitted here for simplicity, and the expressions for extinction cross section σ_{ext} , and scattering cross section σ_{sca} are shown below:

$$\sigma_{ext} = \frac{2\pi}{k_M^2} \sum_{n=1}^{\infty} (2n+1) Re(a_n + b_n) \quad (3.14)$$

$$\sigma_{sca} = \frac{2\pi}{k_M^2} \sum_{n=1}^{\infty} (2n+1) Re(|a_n|^2 + |b_n|^2) \quad (3.15)$$

And the absorption cross section is simply:

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca} \quad (3.16)$$

The efficiencies Q_{ext} , Q_{sca} and Q_{abs} are simply obtained by dividing equations (3.14), (3.15) and (3.16) by πR^2 respectively.

Mie's extension to multi-shelled sphere

The cross sections of scattering, absorption and extinction can be calculated by an extension of the Mie theory for single homogeneous sphere: The final expressions of a multi-shelled sphere for extinction, scattering and absorption cross sections as well as efficiencies are the same for the single homogeneous sphere as described by equations (3.14) (3.15) and (3.16), except that the expansion coefficients a_n and b_n are modified.

Consider a multi-shelled sphere consisting of $r - 1$ concentric shells of arbitrary material and of different thickness d_s , $s = 2, 3 \dots, r$, and a spherical core with radius $R_{core}(s = 1)$, as shown in Figure 3.5.³⁰ The core's refractive index n_1 , and each shell's refractive index n_s are generally complex. The embedding medium is assumed to be non-absorbing with a refractive index of n_M . Illuminated by an incident plane wave with wavelength λ , the wavenumber is $k_M = (2\pi n_M)/\lambda$. The relative refractive index from shell s to $s + 1$ is represented by $m_s = n_s/n_{s+1}$. When $s = r$, n_{s+1} is the surrounding medium's refractive index n_M . The wavenumber in shell s is $k_s = (2\pi n_s)/\lambda$. The size parameter of the sphere containing up to shell s is given by:

$$x_s = k_{s+1} \left(R_{core} + \sum_{j=2}^s d_j \right) \quad (3.17)$$

Figure 3.5 Multi-shelled sphere with $r - 1$ shells. Figure is taken from reference.³⁰

The mathematical procedures also follow that for a single homogeneous sphere. At the first stage, electromagnetic waves of incidence, scattered, in the core and in each shell, are expressed in terms of vector harmonics. The expansions for waves of incidence, scattered and in the core, are the same for that of single homogeneous sphere, as given by equations (3.5) (3.6) and (3.7). The expansions for waves in each shell are given below:

$$E_s = E_0 \sum_{n=1}^{\infty} \frac{i^n (2n+1)}{n(n+1)} \left\{ \left[\beta_n^s M_{on1}^{(1)}(k_s) + \delta_n^s M_{on1}^{(2)}(k_s) \right] - i \left[\alpha_n^s N_{en1}^{(1)}(k_s) + \gamma_n^s N_{en1}^{(2)}(k_s) \right] \right\} \quad (3.18a)$$

$$H_s = \frac{-k_s E_0}{\omega \mu_0} \sum_{n=1}^{\infty} \frac{i^n (2n+1)}{n(n+1)} \left\{ \left[\alpha_n^s M_{en1}^{(1)}(k_s) + \gamma_n^s M_{en1}^{(2)}(k_s) \right] + i \left[\beta_n^s N_{on1}^{(1)}(k_s) + \delta_n^s N_{on1}^{(2)}(k_s) \right] \right\} \quad (3.18b)$$

where α_n^s , γ_n^s , β_n^s and δ_n^s are the expansion coefficients in the shell s ($s > 1$). The superscript of the vector harmonics indicates the kind of spherical function represented by z_n : ‘1’ stands for spherical Bessel functions j_n , ‘2’ stands for the spherical Neumann functions Y_n .

Then, at stage 2, the Maxwell’s boundary condition is applied at each interface between two media. Starting from the innermost boundary, the step-by-step resolution of the boundary conditions leads to the expressions for scattering expansion coefficients a_n and b_n as shown below for a multi-shelled sphere with $r - 1$ shells:

$$a_n = \frac{\psi_n(x_r) [\psi'_n(m_r x_r) + S_n^{r-1} \chi'_n(m_r x_r)] - m_r \psi'_n(x_r) [\psi_n(m_r x_r) + S_n^{r-1} \chi_n(m_r x_r)]}{\xi_n(x_r) [\psi'_n(m_r x_r) + S_n^{r-1} \chi'_n(m_r x_r)] - m_r \xi'_n(x_r) [\psi_n(m_r x_r) + S_n^{r-1} \chi_n(m_r x_r)]} \quad (3.19)$$

$$b_n = \frac{m_r \psi_n(x_r) [\psi'_n(m_r x_r) + T_n^{r-1} \chi'_n(m_r x_r)] - \psi'_n(x_r) [\psi_n(m_r x_r) + T_n^{r-1} \chi_n(m_r x_r)]}{m_r \xi_n(x_r) [\psi'_n(m_r x_r) + T_n^{r-1} \chi'_n(m_r x_r)] - \xi'_n(x_r) [\psi_n(m_r x_r) + T_n^{r-1} \chi_n(m_r x_r)]} \quad (3.20)$$

with

$$S_n^s = \frac{\psi_n(x_s) [\psi'_n(m_s x_s) + S_n^{s-1} \chi'_n(m_s x_s)] - m_s \psi'_n(x_s) [\psi_n(m_s x_s) + S_n^{s-1} \chi_n(m_s x_s)]}{\chi_n(x_s) [\psi'_n(m_s x_s) + S_n^{s-1} \chi'_n(m_s x_s)] - m_s \chi'_n(x_s) [\psi_n(m_s x_s) + S_n^{s-1} \chi_n(m_s x_s)]} \quad (3.21)$$

$$T_n^s = \frac{m_s \psi_n(x_s) [\psi'_n(m_s x_s) + T_n^{s-1} \chi'_n(m_s x_s)] - \psi'_n(x_s) [\psi_n(m_s x_s) + T_n^{s-1} \chi_n(m_s x_s)]}{m_s \chi_n(x_s) [\psi'_n(m_s x_s) + T_n^{s-1} \chi'_n(m_s x_s)] - \chi'_n(x_s) [\psi_n(m_s x_s) + T_n^{s-1} \chi_n(m_s x_s)]} \quad (3.22)$$

and the initiating values are $S_n^0 = T_n^0 = 0$. $\psi_n(x) = x j_n(x)$, $\chi_n(x) = x \gamma_n(x)$, and $\xi_n(x) = x h_n^{(1)}(x)$ are Riccati-Bessel, Riccati-Neumann and Riccati-Hankel functions respectively.

Lastly, at stage 3, cross sections σ_{ext} , σ_{sca} and σ_{abs} as well as their corresponding efficiencies are obtained by substituting equations (3.19) and (3.20) into equations (3.14) and (3.15).

3.1.2 Finite Difference Time Domain (FDTD)

The central idea behind FDTD is to approximate derivative of a function $f(x)$ with respect to x by equation (3.23), so that the first-order derivatives with respect to time and space appearing in Maxwell's equations can be approximated numerically and the fields at each point of the space can be computed by a time marching scheme.⁸⁰

$$\frac{df(x)}{dx} \cong \frac{f\left(x + \frac{\Delta x}{2}\right) - f\left(x - \frac{\Delta x}{2}\right)}{\Delta x} \quad (3.23)$$

where Δx is a positive small step of the variable x . To enable numerical approximation of space-related first order derivatives in Maxwell's equations, the FDTD method discretizes the entire space of interest which contains the nanoparticles to be simulated. Each element of the discretized space is called a Yee Cell,⁸¹ proposed by K. S. Yee, and is shown in Figure 3.6.

Figure 3.6 Schematic of Yee Cell (the bigger cube) which is the base element of the discretized space by FDTD method. The smaller cube's edge length is half of that of the bigger cube. Spatial locations of one Yee Cell's components of electric field (denoted by E_x , E_y or E_z) and magnetic field (denoted by H_x , H_y or H_z) are on the six

vertices of the smaller cube as shown in figure. The edge lengths of a Yee Cell along x -, y - and z - directions do not necessarily have to be equal, but FDTD would be more numerically robust if they are equal. Figure is taken from reference.⁸²

Utilization of Yee Cell as base element to discretize spatial space in FDTD method has three advantages:⁸²

1. The two divergence equations in Maxwell's equations (i.e., $\nabla \cdot (\epsilon \vec{E}) = 0$ and $\nabla \cdot (\mu \vec{H}) = 0$) are automatically satisfied.
2. Physical boundary conditions (i.e., tangential components of electric and magnetic field are continuous at interface) are naturally satisfied.
3. It provides an elegant arrangement for further formulation according to Maxwell's curl equations.

Since the two divergence equations in Maxwell's equations are automatically satisfied with the utilization of Yee Cell, FDTD is formulated from the two curl equations in Maxwell's equations as shown below:

$$\nabla \times \vec{E}(t) = -\mu \frac{\partial \vec{H}(t)}{\partial t} \quad (3.24)$$

$$\nabla \times \vec{H}(t) = \epsilon \frac{\partial \vec{E}(t)}{\partial t} \quad (3.25)$$

where $\vec{E}(t)$ and $\vec{H}(t)$ are the vector forms of electric and magnetic fields, respectively; μ and ϵ are material's permeability and permittivity, respectively; t denotes current time. The expansion from the vector form of equation (3.24) is shown as equation (3.26), and the expansion from the vector form of equation (3.25) is shown as equation (3.27).⁸²

$$\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} = -\mu \frac{\partial H_x}{\partial t} \quad (3.26a)$$

$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = -\mu \frac{\partial H_y}{\partial t} \quad (3.26b)$$

$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = -\mu \frac{\partial H_z}{\partial t} \quad (3.26c)$$

$$\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} = \varepsilon \frac{\partial E_x}{\partial t} \quad (3.27a)$$

$$\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = \varepsilon \frac{\partial E_y}{\partial t} \quad (3.27b)$$

$$\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = \varepsilon \frac{\partial E_z}{\partial t} \quad (3.27c)$$

where x , y and z are coordinates on the x-, y- and z- axes of the cartesian coordinate system shown by Figure 3.6; E_x , E_y and E_z are the three components of electric field which are shown in Figure 3.6, while H_x , H_y and H_z are the three components of magnetic field which are shown in Figure 3.6. So, if we approximate derivative appearing in equation (3.26) and equation (3.27) using the method described by equation (3.23) the following equations can be written:

$$\frac{E_z^{i,j+1,k}|_t - E_z^{i,j,k}|_t}{\Delta y} - \frac{E_y^{i,j,k+1}|_t - E_y^{i,j,k}|_t}{\Delta z} = -\mu \frac{H_x^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_x^{i,j,k}|_{t-\frac{\Delta t}{2}}}{\Delta t} \quad (3.28a)$$

$$\frac{E_x^{i,j,k+1}|_t - E_x^{i,j,k}|_t}{\Delta z} - \frac{E_z^{i+1,j,k}|_t - E_z^{i,j,k}|_t}{\Delta x} = -\mu \frac{H_y^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_y^{i,j,k}|_{t-\frac{\Delta t}{2}}}{\Delta t} \quad (3.28b)$$

$$\frac{E_y^{i+1,j,k}|_t - E_y^{i,j,k}|_t}{\Delta x} - \frac{E_x^{i,j+1,k}|_t - E_x^{i,j,k}|_t}{\Delta y} = -\mu \frac{H_z^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_z^{i,j,k}|_{t-\frac{\Delta t}{2}}}{\Delta t} \quad (3.28c)$$

$$\begin{aligned} & \frac{H_z^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_z^{i,j-1,k}|_{t+\frac{\Delta t}{2}}}{\Delta y} - \frac{H_y^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_y^{i,j,k-1}|_{t+\frac{\Delta t}{2}}}{\Delta z} \\ &= \varepsilon \frac{E_x^{i,j,k}|_{t+\Delta t} - E_x^{i,j,k}|_t}{\Delta t} \end{aligned} \quad (3.29a)$$

$$\begin{aligned} & \frac{H_x^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_x^{i,j,k-1}|_{t+\frac{\Delta t}{2}}}{\Delta z} - \frac{H_z^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_z^{i-1,j,k}|_{t+\frac{\Delta t}{2}}}{\Delta x} \\ &= \varepsilon \frac{E_y^{i,j,k}|_{t+\Delta t} - E_y^{i,j,k}|_t}{\Delta t} \end{aligned} \quad (3.29b)$$

$$\begin{aligned} & \frac{H_y^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_y^{i-1,j,k}|_{t+\frac{\Delta t}{2}}}{\Delta x} - \frac{H_x^{i,j,k}|_{t+\frac{\Delta t}{2}} - H_x^{i,j-1,k}|_{t+\frac{\Delta t}{2}}}{\Delta y} \\ & = \varepsilon \frac{E_z^{i,j,k}|_{t+\Delta t} - E_z^{i,j,k}|_t}{\Delta t} \end{aligned} \quad (3.29c)$$

where Δx , Δy and Δz are the step size along the x-, y- and z- directions in the cartesian coordinate system shown in Figure 3.6, respectively; Δt is the step size of time marching; i , j and k are the coordinates of the current Yee Cell along x-, y- and z- directions in the cartesian coordinate system shown in Figure 3.6, respectively, and i , j , k are integers.

And with equation (3.28) and equation (2.39), FDTD can be implemented: given an initial condition of $\vec{E}$ (i.e., values of $E_x^{i,j,k}|_{t=0}$, $E_y^{i,j,k}|_{t=0}$ and $E_z^{i,j,k}|_{t=0}$ are known at all combinations of i, j, k), equation (3.28) is used to calculate values of $\vec{H}$ at $t = \Delta t/2$ (i.e., values of $H_x^{i,j,k}|_{t=\Delta t/2}$, $H_y^{i,j,k}|_{t=\Delta t/2}$ and $H_z^{i,j,k}|_{t=\Delta t/2}$ are calculated for all Yee Cells that discretise the space of interest); then, with values of $\vec{H}$ at $t = \Delta t/2$, equation (3.29) is used to calculate values of $\vec{E}$ at $t = \Delta t$; then with values of $\vec{E}$ at $t = \Delta t$, equation (3.28) is used to calculate values of $\vec{H}$ at $t = 3\Delta t/2$; then with values of $\vec{H}$ at $t = 3\Delta t/2$, equation (3.29) is used to calculate values of $\vec{E}$ at $t = 2\Delta t$ This time marching scheme goes forward iteratively for $\vec{E}$ and $\vec{H}$ until values of $\vec{E}$ (or $\vec{H}$) converge.

Since each Yee Cell can have a different value of permittivity, an arbitrarily-shaped nanoparticle can be simulated. And from the field values of the simulated spatial region, cross sections of light scattering, absorption and extinction can be calculated.⁸³

3.2 Method to measure material's refractive index

The simulation methods reviewed in Section 3.1 all need material's wavelength-dispersive refractive index (or dielectric function, which is square of refractive index) as one of the inputs. Although material's refractive index can be looked up from literature, it is still important to know how to measure it experimentally. This is because experimentally synthesized material's refractive index generally deviates (maybe not very much) from those reported in literature. For example, refractive indexes of thin-film state metals are generally different from those of their corresponding bulk material due to enhanced surface scattering,⁸⁴⁻⁸⁵ or grain boundary scattering.⁸⁶ And for dielectric material such as TiO₂, its refractive index is sensitive to material's density, which is in turn affected by parameters such as temperature and pressure during deposition process.⁸⁷ A general representation of refractive index is a complex number $N(\omega)$ given in equation (3.30):³⁰

$$N(\omega) = n(\omega) + ik(\omega) \quad (3.30)$$

where n is the traditional refractive index of a non-absorbing material such as glass; k is called the extinction coefficient; and i is the imaginary number; ω is the angular frequency of the incident light. And the relation between material's complex refractive index $N(\omega)$ and its dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is given in equation (3.31):

$$\varepsilon(\omega) = N(\omega)^2 \quad (3.31)$$

The most popular methods to measure material's refractive index n and extinction coefficient k are the Spectroscopic Ellipsometry (SE),⁸⁸ and methods based on film's transmittance and reflectance.⁸⁹⁻⁹⁰ But since SE is more accurate, it is utilized in Chapter 7 to measure TiO₂'s refractive index and is briefly reviewed in this section.

Ellipsometry is an optical measurement technique that characterizes change of linearly polarized light upon reflection from samples.⁹¹⁻⁹² The incident light is linearly polarized, and can be decomposed into p- (parallel to plane of incidence) and s-polarized

(perpendicular to plane of incidence) components, as shown in Figure 3.7.⁹³ Before reflection, the incident wave's p- and s- wave have the same amplitude and are in phase. After reflection from the sample, p- and s- components will go through different amplitude and phase changes, with $\tan\psi$ denoting the ratio of p-component's amplitude over that of s-component, and Δ denoting the difference between p- and s-components' phases. Since the amplitude and phase change of p- and s-component are decided by the n , k values as well as thickness of the sample, n , k values and thickness of the sample can be deduced from the measured spectrum of ψ and Δ .

Figure 3.7 Schematic illustration of SE measurement, and physical meanings of the measured values. Figure is taken from reference.⁹³

The process of deduction of the thin film's (i.e., the sample) complex refractive index and thickness is not analytical, meaning it is difficult to express the thin film's thickness and complex refractive index in terms of ψ and Δ . Instead, appropriate dielectric function models are constructed for different kind of materials,⁹⁴⁻⁹⁶ and calculate the $\hat{\psi}$ and $\hat{\Delta}$ spectrums with an initial guess of model's fitting parameters and film thickness. Then compute the errors between the calculated values of $\hat{\psi}$ and $\hat{\Delta}$ to those of the measured ψ and Δ , and tune the corresponding model's fitting parameters to decrease the error. This tuning process is iteratively carried out until the error between the

calculated values of $\hat{\psi}$ and $\hat{\Delta}$ to the measured values of ψ and Δ is smaller than an acceptable value. At last, the n, k values generated by this tuned dielectric function model is taken as those of the sample's constituent material.

Chapter 4. Frequency-selective scattering by core-shell structure of Ag@TiO₂

4.1 Introduction

Frequency-selective scattering of red, green and blue light based on spherical nanoparticle has the following advantage: spherical nanoparticle is highly symmetric, and therefore does not need any requirement for polarization of incident light and alignment of nanoparticles when dispersed in a transparent matrix. However, as reviewed in Section 2.2, only one spherical structure for frequency-selective scattering has been proposed, which is the spherical core-shell structure of Silica@Ag (Core@Shell).¹³ While designs for frequency-selective scattering of red, green and blue light have been proposed based on the structure of Silica@Ag, as reviewed in part A of Section 2.2, only the one for frequency-selective scattering of blue light has been experimentally realized (Figure 2.12). In addition, thickness-precise coating of Ag shell onto Silica core is difficult to control when the Ag shell's thickness is thin (less than or equal to 20 nm).⁶³ Therefore, it is of interest to look for an experimentally available spherical structure for frequency-selective scattering of green and red light.

In this chapter, nanoparticles in a core-shell structure with silver as the core and TiO₂ as the shell (Ag@TiO₂) are theoretically found to selectively scatter green light while transmitting light of other colours upon proper selection of its core and shell dimensions. This is then experimentally verified by measuring the transmittance, extinction, absorption, and the forward and backward scattering spectrums of a transparent film made by dispersing the Ag@TiO₂ nanoparticles in a polymer matrix. And the film's ability to display a green image is shown visually. The design and simulation for red light scattering are also discussed for completeness.

4.2 Theoretical design for green light scattering

For frequency-selective scattering of green light, the target is to find a nanoparticle that strongly scatters green light (around 530 nm) and transmits light of other colours. In other words, the nanoparticle should have a sharp peak at around 530 nm in the scattering spectrum, with low absorption, and the width of the peak should be as narrow as possible (ideal case is shown in Figure 1.1).

4.2.1 Reasons to choose Ag and TiO₂ to form the core-shell structure

As default in this thesis, I am assuming to achieve this target by taking advantage of metallic nanoparticle's LSPR,^{16-17, 23, 35} whose general properties have been reviewed in Chapter 2. A high frequency-selectivity or sharp scattering peak is desired, and the most appropriate metal is selected from this criterion. The frequency-selectivity can be judged from width of resonance peak, and the narrower the peak width, the higher the frequency-selectivity. Width of resonance peak is given by equation (2.3), and from equation (2.3), it is concluded that metal with smaller imaginary part of its dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ around wavelength of interest (around 530 nm for green light) can generate narrower resonance peak. As alkali metals are very unstable, only noble metals such as Au, Ag, Cu or Al can be considered. Actually, Ag is the best candidate, because near the resonance peak wavelength of 530 nm, the $\varepsilon_2(\omega)$ of Ag is less than 1, while the $\varepsilon_2(\omega)$ of Au, Cu and Al are larger than 2 (Figure 4.1).⁹⁷

Figure 4.1 Imaginary part of the dielectric functions ($\epsilon_2(\omega)$) around 530 nm for Au, Ag, Cu and Al. Optical constants are taken from the literature.³² Figure is taken from reference.⁹⁷

Another way to show sharpness of a peak is through the ratio between on-resonance (at resonant wavelength λ_0) and off-resonance (at $\lambda_0 + \Delta\lambda$, for a small wavelength step $\Delta\lambda$) scattering cross sections,¹³ as given by equation (2.4) reviewed in Chapter 2. And from equation (2.4), it is concluded a small imaginary part ϵ_2 of the metal's dielectric function or a fast-changing real part ϵ_1 of the metal's dielectric function with respect to wavelength (or frequency) generate sharp resonant peak around the wavelength of interest (around 530 nm for green light). A plot of performance estimator $\eta = \left| \frac{d\epsilon_1}{d\lambda} / \epsilon_2 \right|^2$ in visible spectrum range (400 nm ~ 800 nm) for different metals shown in Figure 2.9 also suggests Ag is the best candidate metal to generate a high frequency-selectivity scattering around 530 nm for green light.

According to resonance condition under quasi-static approximation as described by equation (2.2), Ag's resonance wavelength is around 416 nm, assuming the refractive index of the surrounding medium is 1.5 (for most polymer materials). Thus, the next step is to shift the peak wavelength to 530 nm. It has been suggested that both increasing

a metallic nanoparticle's size and coating it with a high-refractive-index dielectric shell will redshift the resonance peak.¹⁶

Increasing the size alone has the following problem: although the dipole-mode resonance peak will redshift, it decreases in strength, and the quadrupole mode will appear and gradually become dominant, resulting in an overall broad extinction spectrum.¹⁶ As shown in equation (4.1), mathematically, the resonance condition for a metallic-core dielectric-shell structure, derived under the quasi-static approximation,³⁰ explains why coating a metallic nanoparticle with a layer of high-refractive-index dielectric shell redshifts the resonance peak:

$$\varepsilon_1(\omega) = -2\varepsilon_{sh} \frac{(\varepsilon_{sh} + 2\varepsilon_m) - \left(\frac{R}{R+d}\right)^3 (\varepsilon_{sh} - \varepsilon_m)}{(\varepsilon_{sh} + 2\varepsilon_m) + 2\left(\frac{R}{R+d}\right)^3 (\varepsilon_{sh} - \varepsilon_m)} \quad (4.1)$$

provided that $\varepsilon_2(\omega)$ is small near the resonance wavelength, where ω is the angular frequency of the incident light; ε_m is the dielectric function of the surrounding medium; ε_{sh} is the dielectric function of the shell (assumed to be constant); and R and d are the core radius and shell thickness, respectively. From equation (4.1), it can be observed that increasing ε_{sh} requires $\varepsilon_1(\omega)$ to be more negative to meet the resonance condition. Since Ag's $\varepsilon_1(\omega)$ decreases with increasing wavelength in the visible spectrum (400 nm–800 nm),³² the resonance peak redshifts when coated with a high-refractive-index dielectric shell. Intuitively, the redshift can be perceived in this way:¹⁶ the dielectric shell reduces the surface charge, due to partial compensation by the polarization of the shell. The reduced surface charge corresponds to a smaller restoring force, which in turn shifts the resonance frequency to lower values. In this work, TiO₂ is selected as the high-refractive index dielectric shell. Thus, a possible nanoparticle that selectively scatters green light is a core-shell structure with Ag as the core and TiO₂ as the shell (Ag@TiO₂).

4.2.2 Optimization consideration

The nanoparticles used in the subsequent experiments were synthesized by a specialized company (nanoComposix) based on our design and simulation results in this section.

The diameter of the Ag core, and the thickness of the TiO₂ shell need to be determined. For this purpose, the figure of merit (*FOM*) defined by equation (2.6) as reviewed in Chapter 2 is used.¹³ As a recap, this *FOM* favours the following properties: a low absorption cross section over the whole visible spectrum, a high scattering cross section at the resonance wavelength, and a low scattering cross section elsewhere, i.e. a sharp scattering peak, with low absorption everywhere.

With this *FOM*, the optimization for Ag@TiO₂ is carried out with the refractive index of the surrounding medium assumed to be $n = 1.5$ (here PVA, polyvinyl alcohol, is used). And TiO₂'s refractive index is assumed to be 1.8. The choice of the value for TiO₂'s refractive index is tentative. The reason why a low refractive index for TiO₂ is chosen rather than a value of 2.7⁹⁸ is that the chemical method employed produces an amorphous TiO₂ shell,⁹⁹ which usually has a much lower refractive index than that of the rutile phase due to its lower density.⁸⁷ Later, it is shown that the actual refractive index of the TiO₂ shell is even lower, down to 1.77, in order to make the calculated spectrum fit the measured extinction spectrum. The choice of Ag's n , k values has to take into account the effect of the surface scattering of electrons, since the size of the silver core is comparable to an electron's mean free path in bulk silver, which is about 52 nm.⁶² The surface scattering of electrons will lead to an increased damping of free electrons. Thus, assuming a silver nanoparticle's dielectric function is represented by a Drude–Lorentz model,¹⁰⁰⁻¹⁰¹ the extra damping γ_s caused by surface scattering of electrons is added to the bulk damping γ_b in the Drude component to give the corrected dielectric function ϵ_c for silver nanoparticles:⁸⁵

$$\varepsilon_C = \varepsilon_{exp} + \frac{\omega_p^2}{\omega(\omega + i\gamma_b)} - \frac{\omega_p^2}{\omega[\omega + i(\gamma_b + \gamma_s)]} \quad (4.2)$$

where ε_{exp} is silver's dielectric function from the literature,³² ω_p is the plasma frequency of silver, ω is the frequency of the incident light, and i is the imaginary number. In the optimization, ω_p and γ_b are assumed to be 9.6 eV and 22.8 meV, respectively.⁸⁵ And γ_s is given by:⁸⁴

$$\gamma_s = \frac{Av_F}{r} \quad (4.3)$$

where $v_F = 1.39 \times 10^6 \text{ m/s}$ is the electron velocity at the Fermi surface for silver,⁸⁵ and r is the radius of the silver core, A is a dimensionless fitting number, whose value is not free from controversy: values from 0.1 to 2 have been justified theoretically.¹⁰² Since A values of 0.25, 0.8 have been experimentally reported,^{84, 102} an A value of 0.5 is chosen for the optimization.

As the silver nanoparticles are readily available from the specialized company with diameters of 5, 10, 20, 25, 30, 40, 50, 60, 70, 75, 80, 100, and 110 nm, the Ag@TiO₂ nanoparticle's core diameters are quantized at these values.

Since the wavelength of green light is around 530 nm, the peak wavelength λ_0 is tuneable from 520 nm to 540 nm. BOBYQA, a local optimization algorithm, is employed in the optimization process.¹⁰³ During the optimization, all diameter values are attempted. At each diameter value, an initial guess for shell thickness is made, and the FOM defined by equation (2.6) is maximized with two tunable variables: the shell thickness and the wavelength (bounded by 520 nm and 540 nm). The result for the optimization is given in Table 4.1. Although a 75 nm silver core with a 7 nm shell has the highest FOM , a TiO₂ shell of 7 nm thickness is difficult to synthesize. So, the structure with the second highest FOM (core = 70 nm, shell = 14 nm) is chosen as the reference target for synthesis. For this chosen reference target, the efficiency spectrums for extinction, scattering and absorption, and a polar diagram of the intensity of the

scattered light at resonant wavelength (525 nm) calculated by the Mie theory are shown in Figure 4.2.

Figure 4.2 (a) Efficiency (defined by $(\text{cross section})/\pi a^2$, where $a = 49 \text{ nm}$) for extinction, scattering and absorption, calculated by the Mie theory for the chosen target structure (core = 70 nm, shell thickness = 14 nm) as a function of wavelength. (b) The blue line represents the intensity of the scattered light at the resonant wavelength (525 nm) plotted against the scattering angle (degrees) in polar form, assuming that the incident light has a unit intensity, and equal components for the p - and s -polarization with respect to the scattering plane. Calculations were done according to the Mie theory. Figure is taken from reference.⁹⁷

Table 4.1 Optimization results. The optimization starts with an initial guess of the shell thickness at each quantized diameter value. Table is adapted from reference.⁹⁷

Diameter (nm)	Initial guess of shell thickness (nm)	Locally optimized shell thickness (nm)	Optimized peak wavelength (nm)	Optimized <i>FOM</i>
40	45	115	527	0.5093
50	35	53	523	0.6541
60	25	42	538	0.8233
70	15	14	525	0.8941
75	10	7	520	0.9087
80	10	4	521	0.8543
100	5	0	540	0.6527

4.3 Experimental verification for green light scattering

The optimized structure (core = 70 nm, shell thickness = 14 nm) serves as a reference target for the experimental synthesis. Due to the difficulty in precisely controlling the size of the core (the core diameter shrinks during synthesis)¹⁰⁴ and the shell, and the uncertainty in the refractive index of amorphous TiO₂ shell caused by its low density,⁸⁷ the optimized size shown in Figure 4.2 cannot be precisely synthesized and even so it may not give a satisfactory spectrum. In fact, of the many samples synthesized, it was found that only the one with an average core diameter of 67 nm and an average shell thickness of 18 nm (Figure 4.3) has satisfactory spectrum characteristics with the peak wavelength at 520 nm, a high scattering cross section around the peak wavelength and a low scattering cross section elsewhere, and an overall low absorption cross section.

Figure 4.3 TEM images of Ag@TiO₂ nanoparticles with an average core diameter of 67 nm, average shell thickness of 18 nm. (a) shows a single particle of such a core-shell structure. In (b), free TiO₂ are observed. Figure is taken from reference.⁹⁷

The Ag@TiO₂ nanoparticles are originally dispersed in IPA (isopropanol) upon receipt, at a concentration of 0.49 mg mL⁻¹. To measure the haze, extinction and transmittance spectrums of the Ag@TiO₂ nanoparticles when their surrounding medium is a polymer matrix, they are dispersed in PVA. The procedures to make an Ag@TiO₂-dispersed PVA film is as follows:

1. Add 3.57 g of PVA (80% hydrolyzed, Sigma-Aldrich) powder in 32 mL of deionized water (PVA has a weight percentage of 10%), and stir for 2–3 hours until PVA is fully dissolved.
2. Degas the PVA water solution, if there are any bubbles, in a vacuum chamber.
3. Add 2 mL of Ag@TiO₂ IPA solution into the PVA water solution and stir for 10 minutes for the nanoparticles to be uniformly dispersed in the solution.
4. Pour the solution obtained into a square glass mould whose size is 10 cm by 10 cm and put the mould in a fume hood for about 3 days.
5. After step 4, the dried PVA film dispersed with Ag@TiO₂ nanoparticles is ready and is torn from the glass mould.

To measure the transmittance, extinction, absorption, scattering, and the ratio of forward and backward scattering of Ag@TiO₂ nanoparticles dispersed in PVA film, a pure PVA film is used for comparison, as described in Section 4.5 “Method”. For the fabrication of the pure PVA film, the procedure is the same as that for the Ag@TiO₂-dispersed PVA film with the exclusion of step 3.

Section 4.5 “Method” describes how to derive the transmittance, extinction, absorption, scattering, and forward and backward scattering spectrums of the Ag@TiO₂-dispersed PVA film from optical measurements.

The transmittance spectrum of the Ag@TiO₂ nanoparticles dispersed in PVA film is measured (normalized against that of the pure PVA film) (Figure 4.4) to show that light with wavelengths in the ranges away from 520 nm has a higher transmittance than that of light with a wavelength near 520 nm.

Figure 4.4 Transmittance of the Ag@TiO₂-dispersed PVA film normalized to the pure PVA film, having an average value of 60.38%. The inset shows the comparison of the transmittance between the Ag@TiO₂-dispersed PVA film and the pure PVA film. Figure is taken from reference.⁹⁷

In Figure 4.5, the measured extinction, absorption, scattering, and forward and backward scattering spectrums are compared to those calculated by the Mie theory. In the calculations, Ag's n , k values were corrected with surface-scattering, as described by equation (4.2) and equation (4.3), assuming the same parameters as in Section 4.2.2 "Optimization consideration" except that the A value is changed to 0.6, and the refractive indices of TiO₂ and the surrounding medium were assumed to be 1.77 and 1.5, respectively. A normal distribution of the nanoparticles with a core diameter of 67 nm with a standard deviation of 17 nm and a shell thickness of 18 nm with a standard deviation of 5 nm were assumed. The method of coating the TiO₂ shell follows that described in the literature.⁹⁹

Figure 4.5 Comparison between measured (red) and calculated (black) extinction spectrums, and components for absorption, and forward and backward scattering calculated by Mie's theory in (a), and those derived from experimental measurements in (b). Note that the sum of the areas of forward and backward scattering gives the total scattering. The way to calculate forward and backward scattering with the Mie theory is to integrate the scattering light power from 0° to 90° and from 90° to 180° with respect to the scattering angle, respectively. The derivation of absorption, and forward and backward scattering from experimental measurements is described in Section 4.5 "Method". The parameters used in the calculations are given in the text. Figure is taken from reference.⁹⁷

The larger measured absorption in Figure 4.5(b), as compared to that calculated in Figure 4.5(a), may be due to absorption of PVA and free TiO₂ particles near the UV region, and a measurement error or a larger damping of electrons' surface scattering (i.e., a larger value of A in equation (6)) in the wavelength region from 420 to 800 nm. The measured back scattering is much smaller than the forward scattering around the resonant wavelength in Figure 4.5(b) as compared to that in Figure 4.5(a). This is due to the specular reflection exclusion port shown in setup $T_5(\lambda)$ (Figure 4.8 below) is very large, so some of the backscattered light is not captured by the integrating sphere. In the region away from the resonant wavelength, since the scattering intensities of the nanoparticles are weak, the measurement of forward and backward scattering is susceptible to noise. A small gap is still observed between the measured and calculated extinction in Figure 4.5, which could be due to the existence of free TiO₂ particles, and particle aggregation.

It is worth mentioning that there are two reasons for which particle aggregation could contribute partially to broadening of resonance peak and cause a negligible redshift of resonance wavelength. The first reason is that aggregated nanoparticles behave as a larger nanoparticle, and according to the Mie theory, this will result in broadening of resonance peak width and a redshift of resonance wavelength, as mentioned in Section 4.2.1. The second reason is that according to studies on plasmonic coupling between metallic nanoparticles,¹⁰⁵⁻¹⁰⁹ certain Fano resonances may occur, depending on inter-particle distances and the relative positions of the metallic nanoparticles in an aggregation. But in the screen shown in Figure 4.6 (a) produced by dispersing Ag@TiO₂ nanoparticles, concentration of Ag@TiO₂ is sparse (9.8 ug/cm²), so aggregation of nanoparticles should be rare. In addition to this, sizes of particle aggregations and relative positions of Ag@TiO₂ particles in an aggregation are rather random. So the individual Fano resonances cannot be observed, and also partially contribute to broadening of resonance peak width.

The effect of the green-light scattering of the Ag@TiO₂-dispersed film is clearly demonstrated by the high quality of the image of the green letters of “NTU” projected onto the film by a laser projector (SONY MP-CL1A), as shown in Figure 4.6(a).

Figure 4.6 (a) Demonstration of the transparent nanoparticle-dispersed PVA film which selectively scatters green light. (b) A pure PVA film without nanoparticles is shown for comparison. The images were projected by a laser projector (SONY MP-CL1A). The images of (a) and (b) are captured with the same lighting and exposure conditions, and the photographs have not been edited. Figure is taken from reference.⁹⁷

The green light generated from this projector is measured to be 523 ± 3 nm. For comparison, the projected image onto the pure PVA film without nanoparticles is also shown in the same figure (Figure 4.6(b)). It can be observed from Figure 4.6(b) that the projected image of the three green letters on the pure PVA film is much poorer. On the other hand, three RGB (red, green and blue) letters of “NTU” were placed behind the Ag@TiO₂-dispersed film. As shown in Figure 4.6, the RGB letters can be clearly observed, showing a reasonably high transparency in the visible wavelength range.

4.4 Theoretical design for red light scattering

It is worth mentioning that the Ag@TiO₂ structure may also be utilized for selective scattering of red light, upon proper selection of core and shell values. An optimization is carried out similar to that described in Section 4.2.2 “Optimization consideration”. All parameters are the same as in the optimization for green light scattering, except that a value of 2 is assumed here for the refractive index of TiO₂, and the tuneable range for peak wavelength λ_0 becomes 620 nm to 650 nm.

The optimized structure has a core diameter of 75 nm, shell thickness of 39 nm, a peak wavelength of 620 nm, with a *FOM* of 0.8921. The efficiency spectrums for extinction, scattering and absorption are plotted in Figure 4.7(a), and a polar diagram of the intensity of the scattered light at the resonant wavelength (620 nm) is plotted in Figure 4.7(b).

Figure 4.7 (a) Efficiency (defined by $(\text{cross section})/\pi a^2$, where $a = 76.5 \text{ nm}$) for extinction, scattering and absorption, calculated by the Mie theory for the structure with the highest FOM (core = 75 nm, shell thickness = 39 nm) as a function of wavelength. (b) The blue line represents the intensity of the scattered light at the resonant wavelength (620 nm) plotted versus the scattering angle (degrees) in polar form, assuming incident light has a unit intensity, and equal components for the p - and s -polarization with respect to the scattering plane. Calculations are done with the Mie theory. Figure is taken from reference.⁹⁷

4.5 Method

The setup to measure transmittance, extinction, absorption, scattering, and forward and backward scattering spectrums with an integrating sphere is an improvement on the one employed in the standard ASTM D 1003,¹¹⁰ and is shown in Figure 4.8, where T_i ($i = 1, 2, 3, 4, 5$) and R is proportional to the amount of light trapped in the integrating sphere, or in other words, the amount of light that fails to leave from the open port at the right-hand side and, in the case of T_5 's setup, the open port for the specularly reflected light

to leave that is near the incident light port.

Figure 4.8 Experimental setup to obtain a film's transmittance, extinction, absorption, scattering, ratio of forward and backward scattering values employing an integrating sphere. The directly measured values are $T_1(\lambda)$, $T_2(\lambda)$, $T_3(\lambda)$, $T_4(\lambda)$, $T_5(\lambda)$ and $R(\lambda)$ where T_i ($i = 1, 2, 3, 4, 5$) or $R(\lambda)$ is proportional to the amount of light trapped in the integrating sphere. The transmittance, extinction, absorption, scattering, ratio of forward and backward scattering values are deduced from these measured values. Figure is taken from reference.⁹⁷

And with the setup shown in Figure 4.8, being similar to (but not the same as) the definition in ASTM D 1003, the haze value here of a film at a wavelength λ is defined as:

$$H(\lambda) = \frac{T_4(\lambda)}{T_2(\lambda)} - \frac{T_3(\lambda)}{T_1(\lambda)} \quad (4.4)$$

The haze value at a wavelength λ given by equation (4.4) shows the proportion of the forwardly scattered light among the total diffusely transmitted light, which consists of forwardly scattered light and directly transmitted light that goes in the same propagating direction of the incident light.

The derivation of nanoparticle's extinction spectrum employs the Beer-Lambert law. Considering the situation shown in Figure 4.9, where $I_n(\lambda)$ ($n = 1,2,3,4$) denotes light intensity, and based on the Beer-Lambert law, the following equation can be obtained:

$$\frac{I_3(\lambda)}{I_2(\lambda)} = e^{-(N \cdot \sigma_{ext} + Noise)} \quad (4.5)$$

where N is the areal density of nanoparticles, i.e. number of nanoparticles per unit area (this area is perpendicular to the propagation direction of the incident light); σ_{ext} is the average extinction cross section of the nanoparticles dispersed in this film; and $Noise$ is due to scattering caused by the non-uniformity of the film itself.

Figure 4.9 Schematic showing light attenuation when going through a thin film. $I_1(\lambda)$ denotes the incident light intensity. $I_2(\lambda)$ denotes the intensity for the light propagating in the original direction after a loss from $I_1(\lambda)$ at the left air / film boundary due to reflectance and surface scattering. $I_3(\lambda)$ denotes the intensity for the light propagating in the original direction after a loss from $I_2(\lambda)$ due to scattering and absorption during the course from the left air / film boundary to the right film / air boundary. $I_4(\lambda)$ denotes the intensity for the light propagating in the original direction after a loss from $I_3(\lambda)$ at the right film / air boundary due to reflectance and surface scattering. Figure is taken from reference.⁹⁷

Assuming that the loss of energy due to reflection and surface scattering at both the left air / film interface and the right film / air interface is x ($0 < x < 1$), we can write the following equations:

$$I_1(\lambda)(1 - x) = I_2(\lambda) \quad (4.6)$$

$$I_3(\lambda)(1 - x) = I_4(\lambda) \quad (4.7)$$

Equation (4.5) can thus be expressed as below in terms of $I_1(\lambda)$ and $I_4(\lambda)$:

$$\frac{I_4(\lambda)}{I_1(\lambda)(1 - x)^2} = e^{-(N \cdot \sigma_{ext} + Noise)} \quad (4.8)$$

As both $I_4(\lambda)$ and $I_1(\lambda)$ are the light intensity in air, they are related to T_i ($i = 1, 2, 3, 4, 5$) by the same proportional constant α as below:

$$I_1(\lambda) = \alpha T_1(\lambda) \quad (4.9)$$

$$I_4(\lambda) = \alpha [1 - H(\lambda)] T_2(\lambda) \quad (4.10)$$

Therefore, equation (4.8) can be written as

$$\frac{[1 - H(\lambda)] T_2(\lambda)}{T_1(\lambda)(1 - x)^2} = e^{-(N \cdot \sigma_{ext} + Noise)} \quad (4.11)$$

Because the loss x and film-dependent *Noise* are unknown, a pure film without any nanoparticle dispersed is used to eliminate the two parameters. A similar expression is derived with the same procedure under the assumption that the two parameters are about the same for the two films:

$$\frac{[1 - H'(\lambda)] T'_2(\lambda)}{T_1(\lambda)(1 - x)^2} = e^{-Noise} \quad (4.12)$$

where $H'(\lambda) \left(= \frac{T'_4(\lambda)}{T'_2(\lambda)} - \frac{T_3(\lambda)}{T_1(\lambda)} \right)$ is the haze value at the wavelength λ of the pure PVA film, $T'_2(\lambda)$ and $T'_4(\lambda)$ are measured for the pure film in the same way as for $T_2(\lambda)$ and $T_4(\lambda)$ for the nanoparticle-dispersed film. Note that $T_1(\lambda)$ and $T_3(\lambda)$ are not affected by the change of sample.

Now, $N \cdot \sigma_{ext}$ can be obtained from (4.11) and (4.12), as given below:

$$N \cdot \sigma_{ext} = -\ln \left(\frac{\left[1 - \left(\frac{T_4(\lambda)}{T_2(\lambda)} - \frac{T_3(\lambda)}{T_1(\lambda)} \right) \right] T_2(\lambda)}{\left[1 - \left(\frac{T'_4(\lambda)}{T'_2(\lambda)} - \frac{T_3(\lambda)}{T_1(\lambda)} \right) \right] T'_2(\lambda)} \right) \quad (4.13)$$

The $N \cdot \sigma_{ext}$, is the total extinction cross section within a unit area, which was also named “extinction constant” in reference.¹⁶ Only $N \cdot \sigma_{ext}$ is derived from experimental measurements. This is because only the overall shape of the $N \cdot \sigma_{ext}$ spectrum that matters. The extinction spectrum $N \cdot \sigma_{ext}$ (red solid line) in Figure 4.5 is normalized such that the maximum value of $N \cdot \sigma_{ext}$ is 1, and the rest values of this spectrum are scaled accordingly.

From Figure 4.9 and equations (4.9) and (4.10), the transmittance shown in the inset of Figure 4.4 is given by the following equation:

$$T(\lambda) = \frac{I_4(\lambda)}{I_1(\lambda)} = \frac{\left[1 - \left(\frac{T_4(\lambda)}{T_2(\lambda)} - \frac{T_3(\lambda)}{T_1(\lambda)} \right) \right] T_2(\lambda)}{T_1(\lambda)} \quad (4.14)$$

To experimentally find the absorption and scattering components from the measured extinction spectrum, $N \cdot \sigma_{abs}$ is firstly derived from measurements in Figure 4.8, where σ_{abs} is the average absorption cross section, in a way similar to that of deriving $N \cdot \sigma_{ext}$ employing Beer-Lambert law. Then, the scattering component is given by $(N \cdot \sigma_{ext} - N \cdot \sigma_{abs})$.

Assuming the PVA film is non-absorptive from 350 nm to 800 nm of light wavelength, then the intensity attenuation of the sum of diffusely transmitted light and diffusely reflected light compared to the incident light after it goes through the sample film is only due to absorption of the dispersed nanoparticles. Thus, with the measurement shown in Figure 4.8, the following equation can be written:

$$\frac{\text{diffusely transmitted light} + \text{diffusely reflected light}}{\text{incident light}} = \frac{T_2(\lambda) + R(\lambda)}{T_1(\lambda)} = e^{-(N \cdot \sigma_{abs} + Noise)} \quad (4.15)$$

where *Noise* comes from the PVA film and measurement system, and in the near UV

region, *Noise* includes PVA film's absorption. Assuming *Noise* in the nanoparticle-dispersed film is the same as in the pure PVA film, the following equation can be written to eliminate the *Noise* in equation (4.15).

$$\frac{T'_2(\lambda) + R'(\lambda)}{T_1(\lambda)} = e^{-Noise} \quad (4.16)$$

where $R'(\lambda)$ is the diffuse reflectance of the pure PVA film measured with the same setup as $R(\lambda)$. Thus, from equations (4.15) and (4.16), $N \cdot \sigma_{abs}$ is given by the following expression:

$$N \cdot \sigma_{abs} = -\ln \left(\frac{T_2(\lambda) + R(\lambda)}{T'_2(\lambda) + R'(\lambda)} \right) \quad (4.17)$$

Thus, the scattering component $N \cdot \sigma_{sca}$, where σ_{sca} is the average scattering cross section, is given by:

$$N \cdot \sigma_{sca} = N \cdot \sigma_{ext} - N \cdot \sigma_{abs} \quad (4.18)$$

Assuming the nanoparticles' forward scattering intensity $I_{Forward Sca}$ is proportional to the right-hand side of the following expression with proportional constant β :

$$I_{Forward Sca} \propto \frac{(H(\lambda) \cdot T_2(\lambda) - H'(\lambda) \cdot T'_2(\lambda))}{T_1(\lambda)} = F \quad (4.19)$$

and the nanoparticles' backward scattering intensity $I_{Back Sca}$ is proportional to the right-hand side of the following expression with the same proportional constant β :

$$I_{Back Sca} \propto \frac{(T_5(\lambda) - T'_5(\lambda))}{T_1(\lambda)} = B \quad (4.20)$$

where $T'_5(\lambda)$ is the pure PVA film's back scattering measured with the same setup as for $T_5(\lambda)$. Then, the ratio of forward scattering $RA_{Forward Sca}$, and of backward scattering $RA_{Back Sca}$ are given by equations (4.21) and (4.22) respectively:

$$RA_{Forward Sca} = \frac{F}{F + B} \quad (4.21)$$

$$RA_{Back\ Sca} = \frac{B}{F + B} \quad (4.22)$$

4.6 Conclusion

In this chapter, Ag@TiO₂ core-shell nanoparticle is proposed and demonstrated to achieve the objective of selectively scattering of green light and red light. A transparent projection film that selectively scatters green light is experimentally realized by dispersing such nanoparticles into a transparent polymer matrix. Since the nanoparticle that enhances blue light scattering has been reported previously,¹³ with the demonstration of selectively scattering of green light in this chapter people are one step closer to achieving a transparent LSPR-based RGB projection display.

Since the scattering peak shown in this work is still not ideally narrow, future works include further reducing the size distribution of the nanoparticle. In next chapter (Chapter 5), effect of surface scattering of free electrons (related to equation (4.2) and equation (4.3)) is demonstrated to be the major contribution that degenerates performance of metallic nanoparticle's frequency-selective scattering, in the sense that it broadens width of resonant scattering peak (therefore decreases frequency-selectivity of light scattering), increases light absorption ratio and decreases light scattering ratio. And in Chapter 6, a remedy is proposed to compensate the negative effect caused by surface scattering of free electrons, by the utilization of gain material.

Chapter 5. Effect of Surface Scattering of Electrons on Ratios of Optical Absorption and Scattering to Extinction of Gold Nanoshell

5.1 Introduction

As indicated by the performance estimator shown in Figure 2.9, gold (Au) is the most promising metallic nanoparticle's constituent material for achieving frequency-selective scattering of red light. According to the resonance condition under quasi-static approximation (equation (2.2)), Au nanoparticle's resonance wavelength is about 540 nm when the surrounding medium has a refractive index of 1.5 (which is the refractive index for most polymers). However, for red light, its wavelength range is about 630 nm to 700 nm,¹¹¹ so it is necessary to redshift Au nanoparticle's resonance wavelength. As shown by part A of Section 2.2 and other literatures, a feasible solution to achieve flexible red-shift of resonance peak is to use the structure of metallic nanoshell (i.e., spherical dielectric core coated with spherical metallic shell), which easily tunes the resonance peak wavelength via the ratio of shell thickness to core diameter.^{13, 112-113} Therefore, Au nanoshell, whose dielectric core could be Silica or Au₂S,^{104, 114} may provide a solution for frequency-selective scattering of red light. Apart from its potential application in a transparent display as frequency-selective light scatterer, Au nanoshell's enhanced light scattering and absorption have found applications in biomedical imaging and photothermal therapy,¹¹⁵⁻¹¹⁶ due to Au's biocompatibility,¹¹⁷⁻¹¹⁸ facile conjugation of antibodies and targeting moieties to Au shell's surface,¹¹⁹ tunability of its resonant wavelength to the near infrared region,^{104, 120} a region called the biological water window where the tissue transmissivity is the highest.¹²¹ As reviewed in Section 3.1, the Mie theory's extension for core-shell structure can be employed to calculate a single Au nanoshell's optical absorption and scattering cross sections,⁵⁸ and the sum of these two gives its extinction cross section. Since the thickness of Au nanoshell is usually smaller than or comparable to electron's mean free

path in bulk Au, which is about 37.7 nm,¹²² electrons in Au shell go through more collisions per unit time (extra collisions are caused by scattering of conduction electrons from shell surface) than they do in bulk Au.^{62, 123} Surface scattering of conduction electrons has been reported to cause broadening of resonance peak, which was verified by fitting of measured and calculated spectra,^{120, 124-126} and reduction in the absolute values of both scattering and absorption of a single nanoshell which was demonstrated by theoretical calculations.^{85, 127-128} However, application of metallic nanoparticle's resonant light scattering in transparent projection display,^{13-15, 97, 129} and in photovoltaics,¹³⁰⁻¹³⁴ require simultaneous high scattering and low absorption ratios at the desired wavelength range. And for scattering-based biomedical imaging applications,^{116, 135-136} where metallic nanoparticles or fluorescent materials are attached to target tissue or cells, if it is desired to only image and not thermally damage the tissue or cells under investigation, it is important that the attached nanoparticle has high ratio in scattering and low ratio in absorption at the desired wavelength. The reason why ratios of scattering and absorption but not their absolute values are of concern is that decrease in absolute values of scattering and absorption can be compensated by having more particles attached to the target tissue or cells. In addition to the above applications, Au metamaterials also require Au to be of the form of thin film, which can achieve high optical absorption as light absorber,¹³⁷⁻¹³⁸ or high transmittance as transparent conducting film,¹³⁹⁻¹⁴² and thus, conduction electrons' surface scattering effect plays a role too. Therefore, it may give some guidance on designing nanoscale Au-related structure to investigate the effect of surface scattering of free electrons on the ratios of optical absorption and scattering to extinction for Au nanoshells.

In this chapter, simulations are first conducted to study the effect of surface scattering of electrons on the ratios of optical absorption and scattering to extinction of Au nanoshells by considering the situations with and without the surface scattering. It is shown that the electrons' surface scattering increases the optical absorption ratio and therefore decreases the light scattering ratio, and the thinner the shell thickness, the

larger the increase in the optical absorption ratio. The increased absorption is then verified experimentally for three samples by comparing their measured and simulated absorption as well as extinction spectra.

The simulation and experimental results will be shown first in Section 5.2: “Results and Discussion”. And then, detailed method of optical measurements of extinction and absorption is provided in Section 5.3: “Methods/Experimental”. The reasons why I want to describe methods of measuring light extinction and absorption spectrums in this chapter again (one version has been described in Chapter 4) are that compared to those described in Section 4.5, in this chapter the method of measuring extinction spectrum is simplified, and additional correction has been considered into measured absorption spectrum for a better fitting with results from simulations. And Section 5.3 can be understood independently without knowledge from Chapter 4.

5.2 Results and Discussion

Au nanoshells with four different shell thicknesses but same core diameter are studied by simulation. The Au nanoshells include (80-nm-diameter Silica core)@(15-nm-thick Au shell), (80-nm-diameter Silica core)@(25-nm-thick Au shell), (80-nm-diameter Silica core)@(35-nm-thick Au shell), and (80-nm-diameter Silica core)@(45-nm-thick Au shell).

The extinction and absorption efficiencies without consideration of surface scattering effect are calculated by using bulk Au’s dielectric function³² as input to the Mie theory, and they are shown as red lines (solid or dashed) in Figure 5.1.

To take into account the effect of surface scattering, equation (4.2) is used again. But for convenience of reading, I will assume that readers do not have knowledge of modelling of surface scattering from Chapter 4. To incorporate effect of surface scattering of free electrons, it is assumed that the dielectric function of Au has a Drude

model component to describe the behaviour of free electrons,¹⁴³ and an extra damping term γ_s contributed by surface scattering of conduction electrons is added to the bulk damping γ_b in the Drude term to give the corrected dielectric function ε_{sh} for Au shell.⁸⁵

$$\varepsilon_{sh} = \varepsilon_{exp} + \frac{\omega_p^2}{\omega(\omega + i\gamma_b)} - \frac{\omega_p^2}{\omega[\omega + i(\gamma_b + \gamma_s)]} \quad (5.1)$$

where ε_{exp} is Au's bulk dielectric function from reference,³² ω_p is the plasma frequency of Au, ω is the frequency of the incident light, i is the imaginary number. For the calculated efficiencies with surface scattering effect in Figure 5.1 (blue lines, solid or dashed), ω_p and γ_b are assumed to be 8.55 eV and 18.4 meV respectively.⁸⁵ And γ_s is given by:⁸⁵

$$\gamma_s = \frac{v_F}{L_B} \quad (5.2)$$

where v_F is the Fermi velocity of electrons in Au, and is equal to $1.40 \times 10^6 \text{ m/s}$,⁸⁵ and L_B is the effective mean free path of the electrons in the shell, derived by assuming billiard scattering model,¹²³ in which the reflections of electrons from the two surfaces of shell are specular, and is given by:

$$L_B = \frac{4(r_o^3 - r_i^3)}{3(r_o^2 + r_i^2)} \quad (5.3)$$

where r_o and r_i are the outer and inner radius of the nanoshell respectively. The refractive indexes of the surrounding medium and Silica core are assumed to be 1.5 and 1.45 respectively.

Figure 5.1 Calculated extinction and absorption efficiencies with and without consideration of surface scattering of conduction electrons, where Q_{ext} stands for extinction efficiency, and Q_{abs} stands for absorption efficiency. The scattering efficiency is the difference between the Q_{ext} and Q_{abs} . All calculations are carried out by Mie theory, with Silica and surrounding medium's indices assumed to be 1.45 and 1.5 respectively. Au's dielectric constants without surface scattering is from reference,³² while that with surface scattering is given by equations (5.1)~(5.3). (a) is for (80 nm diameter Silica core)@(15 nm thickness Au shell); (b) is for (80 nm diameter Silica core)@(25 nm thickness Au shell); (c) is for (80 nm diameter Silica core)@(35 nm thickness Au shell); and (d) is for (80 nm diameter Silica core)@(45 nm thickness Au shell). Figure is adapted from reference.⁶¹

From Figure 5.1, for the four shell thicknesses, after including the surface scattering effect, it is observed that both the extinction and absorption spectrums experience a broadening, and that while the extinction spectrums decrease in magnitude, the

absorption spectrums increase a lot at the dipolar resonance peak (the peak between 700 nm and 800 nm) and seems to not change at the quadrupolar resonance peak (the peak between 550 nm and 600 nm). The decrease in extinction efficiency magnitude and increase in absorption efficiency magnitude lead to increase in the ratio of absorption to extinction, after inclusion of the surface scattering effect. Intuitively, the increase in absorption ratio after considering surface scattering effect becomes less significant with increasing shell thickness, as can be observed from Figure 5.1. This is because the thicker the shell, the less the frequency of electrons' collisions with the shell surfaces, i.e., surface scattering effect is reduced. The phenomenon is also confirmed by Table 5.1. For each shell thickness, the absorption ratio with (without) surface scattering, calculated by the ratio of the region under the blue (red) dashed-curve to the region under the blue (red) solid-curve, is tabulated in Table 5.1. To further investigate the mechanism behind the increase of absorption ratio, spatial distributions of square of near electric field amplitude $|E|^2$ are plotted in Figure 5.2.

Table 5.1 Comparison of the absorption ratio between the calculations with and without the surface scattering effect of conduction electrons. The results are obtained from Figure 5.1. Table is taken from reference.⁶¹

Shell thickness	15 nm	25 nm	35 nm	45 nm
Absorption ratio without surface scattering effect	25.92%	20.52%	17.83%	16.41%
Absorption ratio with surface scattering effect	45.30%	28.72%	22.30%	19.49%
Relative increase of absorption ratio	74.77%	39.96%	25.07%	18.77%

Figure 5.2 $|E|^2$ plots of the four structures shown in Figure 5.1 at their corresponding dipolar resonance peak wavelengths. (a) and (b) are plotted for (80 nm diameter Silica core)@(15 nm thickness Au shell) at 700 nm; (c) and (d) are plotted for (80 nm diameter Silica core)@(25 nm thickness Au shell) at 684 nm; (e) and (f) are plotted for (80 nm diameter Silica core)@(35 nm thickness Au shell) at 706 nm; (g) and (h) are plotted for (80 nm diameter Silica core)@(45 nm thickness Au shell) at 756 nm. Left column, i.e., (a), (c), (e) and (g) show $|E|^2$ calculated with bulk Au's dielectric constants from reference.³² Right column, i.e., (b), (d), (f) and (h) show $|E|^2$ calculated with Au's dielectric constants modified with surface scattering via equations (5.1)~(5.3). The polarization and the propagating direction of the incident light are same for all figures and are shown in (a). Figure is taken from reference.⁶¹

From Figure 5.2, it can be observed that $|E|^2s$ calculated without surface scattering are larger than those with surface scattering, which may be explained in this way: assuming surface scattering takes effect, conduction electrons experience more collisions from shell surfaces as compared to those in bulk Au, so conduction electrons' average oscillation amplitude is decreased, leading to reduced $|E|^2s$. And since collisions of conduction electrons with shell surfaces contribute to energy loss as heat, the absorption ratio is increased after including surface scattering effect.

Subject to availability of material, absorption and extinction are experimentally measured for 3 nanoshells of different shell thicknesses but similar core diameters: (80 nm diameter Silica core)@(16 nm thickness Au shell), (79 nm diameter Silica core)@(29 nm thickness Au shell), and (88 nm diameter Silica core)@(36 nm thickness Au shell), whose TEM images are shown in Figure 5.3.

Figure 5.3 TEM images of the three Au nanoshells used in experimental measurements. (a) 80 nm diameter Silica core, 16 nm thickness Au shell, (b) 79 nm diameter Silica core, 29 nm thickness Au shell, (c) 88 nm diameter Silica core, 36 nm thickness Au shell. The detailed characterization information is provided in Appendix A. Figure is taken from reference.⁶¹

Figure 5.4 shows the comparison between the experimentally measured and theoretically simulated results for the three nanoshells.

Figure 5.4 Comparisons between measured and calculated absorption spectrums with and without consideration of surface scattering of conduction electrons. All calculations are carried out by Mie theory. The surrounding medium is PVA (polyvinyl alcohol) having a refractive index of 1.5. The surfactants coating the nanoshells can be neglected because the surfactants are thin polymer and have similar refractive index as the surrounding medium of PVA. The refractive index of Silica is assumed to be 1.45 in the calculations. Au's dielectric constants without surface scattering is from reference,³² while that with surface scattering is given by equations (5.1) and (5.4). In all figure legends, "Ext" is short for extinction, "Abs" is short for absorption, and "SC" is short for surface scattering. In each figure, "Ext calculated", and "Abs calculated with SC" are the extinction and absorption spectrums calculated with the fitting parameters shown in Table 5.2, while "Abs calculated without SC" is the absorption cross section calculated without considering size distribution and surface scattering. (a) (80 nm diameter Silica core)@(16 nm thickness Au shell), (b) (79 nm diameter Silica core)@(29 nm thickness Au shell), and (c) (88 nm diameter Silica core)@(36 nm thickness Au shell). Figure is taken from reference.⁶¹

It can be observed in Figure 5.4 that the calculated absorption cross sections with the surface scattering effect taken into account agree well with the measured results for all of the three nanoshells, while there is a large departure between the measured and simulated absorptions if the surface scattering effect is not considered. In Figure 5.4 (b) and (c), the difference between calculated and measured extinction spectrums observed in long wavelength range (750 nm to 900 nm) should be attributed to measurement noise: although a comparison PVA film is synthesized to suppress noise from PVA matrix (detailed discussion is in Section 5.3), the thickness variation and surface roughness of a sample film dispersed with nanoshells are not exactly the same as those of the comparison PVA film. For the nanoshells corresponding to Figure 5.4 (b) and (c), their scattering spectrums are broader in nature compared to that in Figure (a), therefore their light scattering signals are more susceptible to scattering noise resulting from PVA host film's surface roughness and thickness variation. Therefore, it is reasonable to expect that a nanoshell with intrinsic broader resonance peak has a broader measured spectrum than calculated one.

To fit the calculated extinctions (the solid blue lines) to the experimentally measured extinctions (the solid red lines), which are shown in Figure 5.4, the expression of the extra damping γ_s in Equation (5.1) due to surface scattering is given by Equation (5.4) (the same as Equation (4.3)) shown below, replacing Equation (5.2):

$$\gamma_s = \frac{A v_F}{d_s} \quad (5.4)$$

where A is a dimensionless fitting parameter and a larger A indicates a larger damping, d_s is the shell thickness. The fitting parameter A is affected by many factors: electron density at the surface, effect of the interface, anisotropy of particle, quantum mechanical computation, and its value has been shown to range from 0.1 to above 2.¹⁴⁴⁻¹⁴⁵ Note that we can write Equation (5.2) into the form of Equation (5.4) to compare the theoretical value of A predicted by billiard scattering model to those fitted from experiment, by first calculating the value of L_B in Equation (5.2) using Equation

(5.3), and then writing L_B in Equation (5.2) into the form of d_s/A , as shown in Equations (5.5a) to (5.5d) below:

$$\gamma_s = \frac{v_F}{L_B} = v_F \cdot \frac{3(r_o^2 + r_i^2)}{4(r_o^3 - r_i^3)} \quad (5.5a)$$

$$\text{write} \quad \frac{3(r_o^2 + r_i^2)}{4(r_o^3 - r_i^3)} = \frac{A}{d_s} \quad (5.5c)$$

$$\text{then} \quad \gamma_s = \frac{Av_F}{d_s} \quad (5.5c)$$

$$\text{where} \quad A = d_s \cdot \frac{3(r_o^2 + r_i^2)}{4(r_o^3 - r_i^3)} \quad (5.5d)$$

Note that when the shell thickness is less than 25% of the total radius, Equation (5.5d) gives an A value of about 0.5.¹²³ The values of the fitting parameters for the calculated spectrums of the three nanoshells shown in Figure 5.4 are tabulated in Table 5.2.

Table 5.2 Values of the fitting parameters for the calculated spectrums shown in Figure 5.4. Table is taken from reference.⁶¹

Structure	(80 nm diameter Silica core)@(16 nm thickness Au shell)	(79 nm diameter Silica core)@(29 nm thickness Au shell)	(88 nm diameter Silica core)@(36 nm thickness Au shell)
Core diameter (nm)	86	87	89
Shell thickness (nm)	13.5	25	35
A	1.33	1.67	1.33
Standard deviation of core diameter (nm)	4.0	3.4	6.0
Standard deviation of shell thickness (nm)	0.6	1.0	2.3

The calculated extinction and absorption spectrums shown in Figure 5.4, which are normalized to the dipolar peak, have considered the surface scattering and size distribution. For each nanoshell, the standard deviations of the core diameter and shell

thickness are computed respectively by multiplying the core diameter and shell thickness values shown in Table 5.2 with the Coefficient of Variation given in the characterization sheets provided in Appendix A. The core diameters used in the fitting are larger than the values given in the characterization sheets. This is because Silica sphere's size shrinks under TEM examination,¹⁴⁶⁻¹⁴⁷ and the shell thicknesses are obtained by subtracting the core diameters in Table 5.2 from the total diameters given in characterization sheets. The calculated extinction spectrums' peak widths are tuned to match the measured ones, and then the corresponding absorption spectrums are calculated with the tuned parameters. The values of A predicted by billiard scattering model would be 0.60, 0.52 and 0.53 for the three nanoshells respectively if Equation (5.5d) is applied, which are obviously smaller than the fitted A values listed in Table 5.2, which are 1.33, 1.67 and 1.33, respectively for the three nanoshells. Since a larger value of A in Equation (5.4) means a larger damping of free electrons, it is observed that the actual damping of conduction electrons is larger than that predicted by the billiard scattering model, where the extra damping could be due to the chemical interface between the shell and the surrounding medium as well as the Silica core,^{16, 148} electron density at the surface, anisotropy of particle, and quantum mechanical computation, as mentioned earlier. The possibility of discontinuous shell can be excluded by observing the TEM image in the characterization sheet in Appendix A. Note that the peak broadening due to nanoshell's size distribution has already been considered during the fitting, i.e., the fitted values of A does not account for size distribution. The details of how to measure the extinction and absorption are described in next Section: "Methods/Experimental".

5.3 Methods/Experimental

In this section, for the nanoshells studied in Figure 5.4, it is described how to disperse them into PVA (polyvinyl alcohol) thin films and how to derive the extinction and absorption of these nanoshells from optical measurements of the nanoparticle-dispersed PVA thin films.

The three nanoshells studied in Figure 5.4, i.e., (80-nm-diameter Silica core)@(16-nm-thick Au shell), (79-nm-diameter Silica core)@(29-nm-thick Au shell), and (88-nm-diameter Silica core)@(36-nm-thick Au shell), which for convenience are in abbreviation as 16-nm, 29-nm, and 36-nm Au nanoshells respectively in the following discussion, were purchased directly from the specialized company, nanoComposix, and their characterization sheets are shown in Appendix A.

The nanoshells were dispersed in water upon receiving, with the 16-nm Au nanoshell having a concentration of 0.02 mg/mL and the other two having a concentration of 0.05 mg/mL. For the 16-nm, 29-nm, and 36-nm Au nanoshells, 34, 25, and 34 mL of their solutions were used to make the nanoparticle-dispersed PVA film. Before mixing the as-received nanoshell solutions with PVA powder (80% hydrolyzed, Sigma-Aldrich), each nanoshell solution was concentrated to 9 mL by centrifugation and re-dispersion. And then 0.9 g PVA powder was added to each concentrated nanoshell solution, and the mixtures were stirred for 2 h. After this, each stirred solution was debubbled in a vacuum chamber and was then poured into a $5 \times 5 \text{ cm}^2$ glass mould, and the mould was put in a fume hood to let the solution naturally dry. After the solutions were dried, the PVA films were teared from the glass moulds, and they are shown in Figure 5.5. A pure PVA film without any nanoparticle dispersed was made likewise, except that 9 mL of water instead of nanoshell solution was mixed with PVA powder.

Figure 5.5 (a) Film dispersed with 16-nm Au nanoshell. (b) Film dispersed with 29-nm Au nanoshell. (c) Film dispersed with 36-nm Au nanoshell. (d) Pure PVA film. Figure is taken from reference.⁶¹

The extinction cross section σ_{ext} of a nanoshell is linked to direct transmittance T of a thin film of nanoshells through Beer-Lambert law:¹⁶

$$T = e^{-N \cdot \sigma_{ext}} \quad (5.6)$$

where N is the areal density of nanoparticles, i.e. number of nanoshells per unit area (note that this area is perpendicular to the propagation direction of the incident light). The direct transmittance T is obtained by normalizing the measured direct transmittance of a PVA film dispersed with nanoshell to that of the pure PVA film without any nanoparticle dispersed. So $N \cdot \sigma_{ext}$ is given by the following equation:

$$N \cdot \sigma_{ext} = -\ln(T) \quad (5.7)$$

Note that instead of σ_{ext} , only $N \cdot \sigma_{ext}$ is derived from experimental measurements, because it is the overall shape of the spectrum that matters. In Figure 5.4, $N \cdot \sigma_{ext}$ is normalized in a way such that the maximum value of $N \cdot \sigma_{ext}$ of the spectrum is 1.

The absorption cross section σ_{abs} of a single nanoshell is related to the intensity loss of a parallel beam of incident light due to absorption ΔI_{abs} after it passes through a thin film of nanoparticles, based on the Beer-Lambert law:¹⁶

$$\Delta I_{abs} = I_0(1 - e^{-N \cdot \sigma_{abs}}) \quad (5.8)$$

where I_0 is the intensity of the incident light.

So, the next step is to experimentally find attenuation of the incident light only due to nanoparticles' absorption. Equation (5.8) assumes the particle to be purely absorbing.¹⁶ For nanoparticle that absorbs and scatters light simultaneously, Equation (5.8) is not valid because of multiple absorptions. For an ensemble of such nanoparticles, when the incident light first hits a nanoparticle, some rays of the light are absorbed, and some are scattered. But for these scattered rays of light, when they hit more nanoparticles during their way out of the nanoparticles' ensemble, a portion of them are absorbed again, leading to multiple absorptions. Multiple absorptions of the scattered light suggest that by measuring the total amount of light that is not absorbed by the PVA film dispersed with nanoshells, the $N \cdot \sigma_{abs}$ derived according to Equation (5.8) tends to overestimate absorption. However, since the PVA film in our experiments is thin (about 0.3 mm), and the nanoshells' concentration is not high, it is assumed that most of the light undergoes single scattering (and thus single absorption).¹³ With this assumption, the experimental setup using an integrating sphere to measure total amount of light that is not absorbed by the PVA film dispersed with nanoshells is shown in Figure 5.6.

Figure 5.6 Experimental Setup to measure absorption. The directly measured values are $T_1(\lambda)$, $T_2(\lambda)$ and $R(\lambda)$ where T_i ($i = 1, 2$) or $R(\lambda)$ is proportional to the amount of light trapped in the integrating sphere. The absorption is deduced from these measured values. This setup is a simplified version of the one reported in Section 4.5. Figure is taken from reference.⁶¹

In Figure 5.6 T_1 , T_2 or R is proportional to the amount of light trapped in the integrating sphere, i.e., the amount of light that fails to go out from the open port at the right side. In the following discussion, it is assumed that T_1 , T_2 and R are proportional to the light intensity collected by the integrating sphere with the same coefficient α .

Equation (5.8) can be rearranged into $(I_0 - \Delta I_{abs}) = I_0 e^{-N \cdot \sigma_{abs}}$, and its left-hand side represents the total amount of light that is not absorbed after the incident light passes through the sample film. From the measurements in Figure 5.6, we can write the following equations:

$$(I_0 - \Delta I_{abs}) = \alpha(T_2(\lambda) + R(\lambda)) \quad (5.9)$$

$$I_0 = \alpha T_1(\lambda) \quad (5.10)$$

Substituting Equation (5.9) and Equation (5.10) into $(I_0 - \Delta I_{abs}) = I_0 e^{-N \cdot \sigma_{abs}}$, and including a noise term in addition to $N \cdot \sigma_{abs}$, the following equation can be obtained:

$$\frac{T_2(\lambda) + R(\lambda)}{T_1(\lambda)} = e^{-(N \cdot \sigma_{abs} + Noise)} \quad (5.11)$$

where *Noise* is from the PVA matrix. Due to the first reflection of the incident light at the air/PVA interface, about 4% of incident light never enters the thin film (according to Fresnel equations, upon normal incidence at an interface of two different media of indices n_1 (=1 for air) and n_2 (=1.5 for PVA), the reflectance of light R is given by $R = \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2$) and thus Equation (5.11) is modified as:

$$\frac{T_2(\lambda) + R(\lambda) - 0.04T_1(\lambda)}{T_1(\lambda) - 0.04T_1(\lambda)} = e^{-(N \cdot \sigma_{abs} + Noise)} \quad (5.12)$$

Assuming the *Noise* in the pure PVA film without any nanoparticle dispersed is the same as that in the nanoshell-dispersed films, a similar expression can be derived for the pure PVA film:

$$\frac{T'_2(\lambda) + R'(\lambda) - 0.04T_1(\lambda)}{T_1(\lambda) - 0.04T_1(\lambda)} = e^{-Noise} \quad (5.13)$$

where $T'_2(\lambda)$ and $R'(\lambda)$ are measured for the pure PVA film in the same way as $T_2(\lambda)$ and $R(\lambda)$ for the nanoshell-dispersed film respectively.

From Equation (5.12) and Equation (5.13), $N \cdot \sigma_{abs}$ is given by the following expression:

$$N \cdot \sigma_{abs} = -\ln \left(\frac{T_2(\lambda) + R(\lambda) - 0.04T_1(\lambda)}{T'_2(\lambda) + R'(\lambda) - 0.04T_1(\lambda)} \right) \quad (5.14)$$

However, during the fitting to the experimental results, in which the value of A in Equation (5.4) is adjusted such that the peak width of the calculated extinction spectrum fits the measured one, it is found that the normalized $N \cdot \sigma_{abs}$ is still a little bit larger

than the calculated absorption which includes the surface scattering effect. This suggests that multiple absorptions of scattered light may still contribute to extra absorption, as discussed previously. So, it is estimated here that a portion p ($0 < p < 1$) of the scattered light when no multiple absorptions happen is absorbed in the actual situation, where p is estimated to be 10% for the 16-nm nanoshell, and 5% for both the 29-nm and 36-nm. The following two equations are set to account for the multiple scatterings effect:

$$N \cdot \sigma_{abs}' + N \cdot \sigma_{sca}' = N \cdot \sigma_{ext} \quad (5.15)$$

$$N \cdot \sigma_{abs} + (1 - p)N \cdot \sigma_{sca}' = N \cdot \sigma_{ext} \quad (5.16)$$

where $N \cdot \sigma_{abs}'$ and $N \cdot \sigma_{sca}'$ are the light absorption and scattering, respectively, when no multiple absorptions happen; and $N \cdot \sigma_{abs}$, $N \cdot \sigma_{ext}$ are the experimentally measured absorption, extinction given by Equation (5.14), Equation (5.7) respectively. The extinction in Equation (5.15) and Equation (5.16) is the same because multiple scattering does not induce error in the measurement of $N \cdot \sigma_{ext}$. From Equation (5.15) and Equation (5.16), the corrected expression for the measured absorption is given below:

$$N \cdot \sigma_{abs}' = N \cdot \sigma_{ext} - \frac{1}{(1 - p)} (N \cdot \sigma_{ext} - N \cdot \sigma_{abs}) \quad (5.17)$$

In Figure 5.4, the corrected absorption $N \cdot \sigma_{abs}'$ is also normalized to the maximum value of the $N \cdot \sigma_{ext}$ spectrum calculated with Equation (5.7).

5.4 Conclusion

In this chapter, surface scattering of conduction electrons in Au nanoshell is shown to not only broaden the extinction peak width, but also increase the ratio of light absorption to extinction, and thus decrease the ratio of light scattering to extinction. It is also found that the thinner the shell thickness, the more increase of the absorption ratio. And the increase of light absorption ratio is verified by fitting of calculated

absorption spectra to measured ones.

Although this study is only conducted on Au nanoshell, the same conclusion should apply to other metallic nanostructures. So, as long as surface scattering of conduction electrons happen, broadening of resonance peak and decrease of light scattering ratio are inevitable. And these effects are not desirable in frequency-selective scattering to achieve transparent projection display. But in next chapter, it will be shown that these drawbacks caused by surface scattering of conduction electrons can be remedied by combining metallic nanoparticle with gain material.

Chapter 6. Sharp frequency-selective scattering of red, green, and blue light achieved via gain material's loss compensation

6.1 Introduction

As shown in Section 2.2, and Chapter 4, although frequency-selective scattering of red, green and blue light can be achieved by metallic nanoparticle's LSPR, light absorption is inevitable in LSPR peak(s) of a metallic nanoparticle due to metal's optical loss, which is undesirable for scattering-based applications (for instance, transparent projection display as far as this thesis is concerned). In addition, as demonstrated in Chapter 5 and other literatures, since a metallic nanoparticle's size is comparable or smaller than mean free path of electrons in the constituent material, surface scattering of conduction electrons becomes significant,^{62, 68, 149} which undesirably increases light absorption and decreases the frequency-selectivity of light scattering by broadening the LSPR peak width.^{61, 120, 124-126} Nevertheless, these problems may be solved by incorporating gain materials such as rare earth ions and laser dyes, which compensate optical loss and narrow LSPR peak width.^{128, 150-158}

In this chapter, through numerical simulation, the aim is to achieve sharp scattering peaks at red, green and blue light, with low absorption in the visible light range (400 nm ~800 nm) based on metallic nanoparticle's LSPR effect and gain material's loss compensation. Optimizations based on metallic nanosphere, spherical core-shell structures of metal@Silica (core@shell) and Silica@metal are conducted for gold (Au), silver (Ag) and aluminium (Al), with and without gain material. During the optimizations, the effect of surface scattering of conduction electrons is considered. The results from the optimizations show that for the Ag and Au-based structures, introducing gain material significantly improves the scattering behaviour (i.e., there are sharpe scattering peaks at red, green and blue light, respectively, and low absorption over visible light range), however the improvement is not significant for the Al-based

structures. And it is found that the most suitable structures for sharp selective scattering at the red, green and blue light wavelength regions are Silica@Au, Ag@Silica and Silica@Ag, respectively, all with a gain material.

6.2 Simulation method

As a quick recap, in Section 2.1, I have introduced two ways of judging a metal's potential of generating highly frequency-selective light scattering peak, which correspond to Equation (2.3) and Equation (2.4). And based on Equations (2.3) and (2.4), a performance estimator is shown in Figure 2.9. However, since gain material is supposed to be combined with metallic nanoparticle in this chapter, and gain material can compensate optical loss (characterized by imaginary part of a metal's dielectric function around wavelength range of interest), a small imaginary part of metal's dielectric function around wavelength range of interest may not be necessary. Therefore, in this chapter, metals to be employed in subsequent simulations should only satisfy the following condition: their LSPR peak(s) resulting from free electrons' oscillations should be clearly separated from the broad spectrums caused by inter-band transitions of bound electrons³⁰ (i.e., if they overlap, then the peak width is broadened, resulting in a poor frequency-selectivity). According to this criteria, alkali metals, Al, Au and Ag are the candidates. However, alkali metals are excluded because they are very reactive. So, only Al, Au and Ag will be used in the following simulations.

As in Chapter 4, in this chapter, surrounding medium's refractive index is also assumed to be 1.5, which is about the same as the refractive indices of glass and most polymers, in which the nanoparticles to be designed are supposed to be dispersed. So, from Equation (2.2), the resonance condition under quasi-static approximation, resonance peaks of Ag, Au and Al appear at 416 nm, 540 nm and 192 nm respectively, as proven by simulated results shown in Figure 6.1 below.

Figure 6.1 Calculated extinction efficiency spectrum of a single nanosphere with diameter of 10 nm by Mie theory,³⁰ for (a) Ag, (b) Au and (c) Al. The real part of dielectric function is plotted for (d) Ag, (e) Au and (f) Al. The surrounding medium's refractive index is 1.5, so surrounding medium's dielectric function is 2.25, and the resonance peaks appear at the wavelengths at which real part of metals' dielectric function equal to -4.5. The dielectric functions of the metals are from literature.³² Figure is taken from reference.¹⁸

As reviewed in Section 2.1, increasing the metallic nanosphere's size red-shifts its resonance peak, but further decreasing the size of a nanosphere with a size already much smaller than the wavelength of incident light does not significantly blue-shift its resonance peak.¹⁶ Thus, here, the resonance peak wavelengths for Ag, Au and Al spheres in the quasi-static limit are perceived as the lower limits of their corresponding tuning ranges of resonance peak wavelength. The wavelengths of red, green and blue light are around 630 nm, 520 nm and 450 nm, respectively. So, here, Au is considered only for red light scattering, as the lower limit (540 nm) of its resonance-peak-wavelength tuning range is larger than the wavelength of green light, while Ag and Al are considered for scattering of all three colors of light. The next step is to red-shift the metallic nanoparticles' resonance peak wavelengths from their respective ones in the quasi-static limit, to red light for Au, and to all three colors of light for Ag and Al. As demonstrated in Section 2.1, a small red-shift of resonance peak of less than about 50

nm can be achieved by increasing the metallic nanospheres' size. But relying on increasing size to red-shift resonance peak by more than 100 nm has the following problem: the dipole resonance peak's strength will decrease, and the quadruple mode peak will appear and gradually become dominant, undesirably resulting in an overall broad extinction spectrum.¹⁶ Inspired from Section 2.1, Chapter 4 and other literatures, a feasible solution to achieve flexible red-shift of resonance peak is to use the structure of metallic nanoshell (i.e., spherical dielectric core, with concentric spherical metallic shell), which easily tunes the resonance peak wavelength via the ratio of shell thickness to core diameter.^{13, 113, 126} Therefore, the structures of metallic nanosphere and nanoshell are employed in subsequent optimizations when gain material is not included, with the assumption that the dielectric core of nanoshell is Silica. In the case of metallic nanoshell, the gain material is introduced by doping the Silica core with gain material; while in the metallic nanosphere's case, the gain material is introduced by surrounding the metallic nanosphere by a shell of Silica doped with gain material. Experimental realization of doping Silica shell of Au@Silica structure with gain material was demonstrated in a previous work.¹⁵⁹

With the above considerations, the structures to be employed during optimization are summarized in Table 6.1 below and are schematically depicted in Figure 6.2.

(a) Metallic nanosphere (b) Silica/Metal no gain

(c) Metal/Silica with gain (d) Silica/Metal with gain

Figure 6.2 Schematic illustration of the structures to be used during optimization, where metal refers to Ag, Au or Al. The surrounding medium's refractive index is assumed to be 1.5. (a) A single metallic nanosphere. (b) The core-shell structure of “Silica@Metal” without gain material. (c) The core-shell structure of “Metal@Silica”, Silica shell is doped with gain material. (d) The core-shell structure of “Silica@Metal”, Silica core is doped with gain material. Figure is adapted from reference.¹⁸

Table 6.1 Structures on which optimizations are to be performed to search for solutions of sharp selective scattering of red, green and blue light. Table is taken from reference.¹⁸

	Without gain material	With gain material
Red	Au sphere, Silica@Au, Silica@Ag, Silica@Al	Au@Silica, Silica@Au, Silica@Ag, Silica@Al
Green	Ag sphere, Silica@Ag, Silica@Al	Ag@Silica, Silica@Ag, Silica@Al
Blue	Ag sphere, Silica@Ag, Silica@Al	Ag@Silica, Silica@Ag, Silica@Al

For the purpose of optimization, a figure of merit (*FOM*) modified from Equation (2.6) is defined:

$$FOM = \frac{\sigma_{sca}(\lambda_0)}{2\overline{\sigma_{sca}} + \max\{|\sigma_{abs}|\}} \quad (6.1)$$

This *FOM* is the same as the one defined by Equation (2.6) except for the introduction of an absolute value operator on σ_{abs} . Introducing gain material can make the absorption cross section negative, and eventually result in a lasing state¹²⁸ if the absolute value operator is not put on σ_{abs} in Equation (6.1) during optimization of *FOM*. The purpose of introducing gain material is to just compensate light absorption caused by metallic nanoparticle's optical loss, and therefore a low magnitude of overall absorption cross section is preferred over its mathematical value.

Since the size of a metallic nanoparticle is comparable to free electrons' mean free path in the constituent material, effect of surface scattering of conduction electrons on the metal's dielectric function cannot be ignored,⁶² as discussed in Chapter 5. For the structure of metallic nanoshell, i.e., Silica@metal, this issue is taken into account in the same way as in Chapter 5, i.e., through Equations (5.1) to (5.3). While for metallic nanosphere or the Silica-coated metallic nanosphere (i.e., metal@Silica), Equation (5.3) is replaced by Equation (6.2) shown below, i.e., effect of surface scattering of conduction electrons is taken into account through Equations (5.1), (5.2) and (6.2).

$$L_B = \frac{4}{3}r \quad (6.2)$$

where r is the radius of metallic nanosphere or the inner radius of Silica-coated metallic nanosphere and L_B is the effective mean free path of the electrons in the shell. L_B given by Equation (6.2) is derived by setting r_i to 0 in Equation (5.3).

Bulk metal's plasma frequency, damping rate and Fermi velocity of electrons (ω_p , γ_b and v_F) for Ag, Au and Al, respectively, are summarized in Table 6.2.

Table 6.2 Plasma frequencies, damping rates and Fermi velocities of bulk metals used in correcting the metals' dielectric functions for the size effect. Table is taken from reference.¹⁸

	$\omega_p(\text{eV})$	$\gamma_b(\text{eV})$	$v_F(10^6\text{m/s})$
Ag	9.6	0.0228	1.39
Au	8.55	0.0184	1.40
Al	15.3	0.5984	2.03

For Silica without gain material, it is assumed to have a constant refractive index $N_{Si} = 1.45$. For Silica doped with gain material, its refractive index is modelled by:¹²⁸

$$N_{Si} = 1.45 + ik \quad (6.3)$$

where i is the imaginary number, and k is a negative extinction coefficient constant over all wavelengths, since reported gain materials are able to cover the whole visible wavelength range.^{150, 152} Extinction coefficient k is positive for lossy media, 0 for non-absorbing media, and negative for gain media.

Here, Equation (6.3) is a simple assumption, the actual situation is more complicated and are briefly discussed in the following. From a systematic analysis of surface plasmon amplification by stimulated emission of radiation (SPASER),¹⁶⁰⁻¹⁶¹ the gain media provides energy to amplify or to compensate for the loss of the LSPR and, in return, the enhanced near electric field from LSPR exerts periodic perturbation on the gain media causing the feedback for photons in the gain media. Therefore, the value of gain near the metal/gain interface should be different from that away from the interface. And as pointed out by Stockman,¹⁶² the simple model given by Equation (6.3) is only applicable for simulations below the spasing threshold, and more accurate quantum theory should be used for situations above threshold.

The optimization is carried out with BOBYQA,¹⁰³ a local optimization algorithm, which starts from an initial guess of tuning parameters and searches for an optimized set of tuning parameters that give maximum value of FOM . Here, the set of tuning parameters are geometric parameters of the nanostructures shown in Table 6.1 (i.e., core

diameter and shell thickness for metal@Silica and Silica@metal, or diameter for metal sphere), the value of k in Equation (6.3), and resonance peak wavelength λ_0 . The tuning ranges of resonance peak wavelength λ_0 for red, green and blue light are set to be 620 nm to 700 nm, 510 nm to 540 nm, and 440 nm to 460 nm, respectively. The detailed optimization process is as following: for each tuning range of λ_0 , λ_0 is scanned at a step of 1 nm; at each step of λ_0 , BOBYQA is carried out with an initial guess of nanostructure's dimensions and k value; and the set that generates the largest value of FOM defined by Equation (6.1) gives the optimized λ_0 , nanostructure's dimensions and k value. For structures without gain material, k equals to 0 and is not an adjustable parameter during optimization. The optimized results of nanostructure's dimensions, k values and values of optimized FOM are shown in next Section: "Results and discussion."

6.3 Results and discussion

In this section, apart from the optimized tuning parameters, and values of optimized FOM , the calculated optical spectrums are also presented to give an intuitive view of sharp selective scattering.

The spectrums are presented in terms of extinction efficiency (Q_{ext}), scattering efficiency (Q_{sca}) and absorption efficiency (Q_{abs}), whose definitions are given in Section 3.1. For the calculated efficiencies shown in Figures 6.3, 6.4 and 6.5, the Mie theory takes the following parameters as its inputs: the surrounding medium's dielectric function which equals to 2.25, optimized nanostructure's dimensions (i.e., core diameter and shell thickness for a core-shell structure, or diameter for a nanosphere), metal's size-dependent dielectric function, Silica's dielectric function ϵ_{Sil} for the core-shell structure (for a structure without gain material, $\epsilon_{Sil} = N_{Sil}^2 = 2.1025$; for a structure with gain material $\epsilon_{Sil} = N_{Sil}^2 = (1.45 + ik)^2$, where $N_{Sil} = 1.45 + ik$ is from Equation (6.3) and the optimized k is constant over the whole spectrum).

Chapter 6 Sharp Frequency-selective Scattering of Red, Green and Blue Light Achieved via Gain Material's Loss Compensation

Figure 6.3 shows the efficiency spectrums of the structures optimized for selective scattering of red light, and their corresponding values of FOM as well as optimized parameters are shown in Table 6.3.

Table 6.3 Optimized tuning parameters and values of optimized FOM for the structures mentioned in Figure 6.3, with the same alphabetic order. Table is taken from reference.¹⁸

Alphabetic order	Core Diameter (nm)	Shell thickness (nm)	k	Resonance wavelength (nm)	FOM
(a)	101			620	0.7476
(b)	98	5	-0.4663	620	1.1094
(c)	61	23		650	0.7640
(d)	48	10	-1.2888	622	3.17
(e)	65	18		620	0.6063
(f)	56	8	-1.1234	620	1.3391
(g)	97	25		672	0.4509
(h)	83	25	-0.0677	622	0.4853

Figure 6.4 shows the efficiency spectrums of the structures optimized for selective scattering of green light, and their corresponding value of FOM as well as optimized parameters are shown in Table 6.4.

Table 6.4 Optimized tuning parameters and values of optimized FOM for the structures mentioned in Figure 6.4, with the same alphabetic order. Table is taken from reference.¹⁸

Alphabetic order	Core Diameter (nm)	Shell thickness (nm)	k	Resonance wavelength (nm)	FOM
(a)	78			510	0.8163
(b)	78	15	-0.1743	510	1.1289
(c)	20	29		510	0.8087
(d)	34	9	-1.2435	511	2.4128
(e)	65	18		510	0.6329
(f)	62	18	-0.8485	510	0.6522

Figure 6.5 shows the efficiency spectrums of the structures optimized for selective scattering of blue light, and their corresponding value of FOM as well as optimized

parameters are shown in Table 6.5.

Table 6.5 Optimized tuning parameters and values of optimized FOM for the structures mentioned in Figure 6.5, with the same alphabetic order. Table is taken from reference.¹⁸

Alphabetic order	Core Diameter (nm)	Shell thickness (nm)	k	Resonance wavelength (nm)	FOM
(a)	67			460	0.7123
(b)	47	19	-0.1726	443	2.5227
(c)	17	24		460	0.6569
(d)	18	27	-1.44	460	0.6923
(e)	31	23		440	0.9602
(f)	27	26	-0.8688	440	0.9794

Figure 6.3 Efficiency spectrums of optimized structures for selective scattering of red light. The left column, i.e., (a), (c), (e) and (g) are for the optimized structures without gain material, and spectrums of their corresponding structures optimized with gain material are shown in the right column, i.e., (b), (d), (f) and (h). (a) Au sphere without gain. (b) Au@Silica with gain. (c) Silica@Au without gain. (d) Silica@Au with gain. (e) Silica@Ag without gain. (f) Silica@Ag with gain. (g) Silica@Al without gain. (h) Silica@Al with gain. For each structure, the optimized parameters and optimized values of FOM are tabulated in Table 6.3 in the same alphabetic order as their respective structure appears in this figure. Figure is taken from reference.¹⁸

Figure 6.4 Efficiency spectra of optimized structures for selective scattering of green light. The left column, i.e., (a), (c) and (e) are for the optimized structures without gain material, and spectrums of their corresponding structures optimized with gain material are shown in the right column, i.e., (b), (d) and (f). (a) Ag sphere without gain. (b) Ag@Silica with gain. (c) Silica@Ag without gain. (d) Silica@Ag with gain. (e) Silica@Al without gain. (f) Silica@Al with gain. For each structure, the optimized parameters and optimized values of FOM are tabulated in Table 6.4 in the same alphabetic order as their respective structure appears in this figure. Figure is taken from reference.¹⁸

Figure 6.5 Efficiency spectra of optimized structures for selective scattering of blue light. The left column, i.e., (a), (c) and (e) are the optimized structures without gain material, and spectrums of their corresponding structures optimized with gain material are shown in the right column, i.e., (b), (d) and (f). (a) Ag sphere without gain. (b) Ag@Silica with gain. (c) Silica@Ag without gain. (d) Silica@Ag with gain. (e) Silica@Al without gain. (f) Silica@Al with gain. For each structure, the optimized parameters and optimized values of FOM are tabulated in Table 6.5 in the same alphabetic order as their respective structure appears in this figure. Figure is taken from reference.¹⁸

Negative absorption is observed for some structures, which is explained by the concept

of surface plasmon amplification by stimulated emission of radiation.¹⁶⁰ The occurrence of negative absorption is reasonable with the introduction of gain material, as gain material is used in laser to achieve lasing state which is a state of light amplification. One question may occur to reader that why negative absorption is observed only around resonance wavelength, although constant gain over the whole visible spectral range is assumed. A reasonable explanation for this is given as: Around resonant wavelength of light scattering, the coupling of incident light's electric field to the free electrons' oscillation of dipolar plasmon mode is very strong, resulting in a large enhancement of electric field near the surface of metallic nanoparticle, as can be observed in Figure 7.5 and Figure 7.6, or from reference.¹⁷ Therefore, it should be the enhanced near-field around the metallic nanoparticle that stimulates the negative absorption from the adjacent gain material.¹⁶³ And for wavelengths away from the resonance, near-field is very small, so negative absorption is not turned on.

By observing Figures 6.3, 6.4 and 6.5, it is obvious that Al-based structures are not suitable for selective scattering, since their resonance peaks are too broad, even though absorptions are low. The efficiency spectrums for Al-based structures do not show apparent improvements even after gain material is introduced. And the broad resonance peaks for Al-based structures can be explained by Al's low quality factor, which determines strength of resonance, defined by $-\varepsilon_1(\omega)/\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary part of Al's dielectric function, over the whole visible wavelength range.⁸⁵

Apart from structures of Al, by comparing the calculated efficiency spectrums of the structures without gain material to those of structures with gain material in Figures 6.3, 6.4 and 6.5, it is observed that introducing gain material significantly improves the scattering quality in the sense that the ratios of absorption are decreased, and the resonance scattering peaks become sharper. And the improvements after introducing gain material are confirmed by the increase of values of *FOM* as shown in Tables 6.3,

6.4 and 6.5.

The largest values of FOM in Tables 6.3, 6.4 and 6.5 (3.17, 2.4128 and 2.5227 respectively) suggest that the most suitable structures for sharp selective scattering of red, green and blue light are Silica@Au with gain material (see Table 6.3), Silica@Ag with gain material (see Table 6.4), and Ag@Silica with gain material (see Table 6.5), respectively. Their angular distributions of scattering are shown in Figure 6.6. The results shown in Figure 6.6 suggest that the scattered light can be viewed from a wide range of angle. The FOM values of the most suitable structures are much larger than those reported in previous works as reviewed in Section 2.2 and Chapter 4,^{13, 15, 97} as appreciated from Table 6.6, showing a great improvement in selective scattering of red, green and blue light.

Table 6.6 Comparison of optimized values of FOM from this work to those from previous works for red, green and blue light. Table is taken from reference.¹⁸

	Red	Green	Blue
This work	3.17	2.4128	2.5227
Previous works	1.6	1.1	1.01

Figure 6.6 Intensity of the scattered light at the resonant wavelengths versus the scattering angle (in the unit of degree) in polar form for the most suitable structures respectively for selective scattering of red, green and blue light: (a) Silica@Au with gain material (Table 6.3), (b) Silica@Ag with gain material (Table 6.4), and (c) Ag@Silica with gain material (Table 6.5). The incident light has a unit intensity and equal intensity for the p - and s - components with respect to the scattering plane. Calculations are carried out with the Mie theory. Figure is taken from reference.¹⁸

Among the three most suitable structures, the one for selective scattering of red light, i.e., the structure of Silica@Au with gain material (item d in Table 6.3), has the largest magnitude of optimized k which is 1.2888, and this corresponds to a gain value of $2.6 \times 10^5 \text{ cm}^{-1}$, according to the relation $\text{gain} = -4\pi k/\lambda$,¹⁵⁰ where $\lambda = 622 \text{ nm}$ is this structure's optimized resonance wavelength. The relation between gain and the emission cross section σ_e of a single gain material (dye or rare earth ion) is: $\text{gain} = \rho \cdot \sigma_e$,¹⁵³ where ρ is gain material's volume concentration. The usually-known gain material's emission cross section is of the order of 10^{-16} cm^2 ,^{150-151, 153} which

corresponds to a maximum gain of the order of 10^3 cm^{-1} . However, it has been pointed out that the theoretical limit of emission cross section set by quantum mechanics is $3\lambda^2/(2\pi)$,¹⁶⁴ which is of the order of 10^{-10} cm^2 for visible wavelength range, and is 6 orders larger than 10^{-16} cm^2 . So, a gain value of the order of 10^5 cm^{-1} may be achieved theoretically.

Figure 6.7 Simulated transmittance of a film dispersed with the three most suitable structures. Densities of the three structures are chosen such that transmittance at their corresponding resonance wavelengths become 20%. Surrounding medium is assumed to have a refractive index of 1.5. Average transmittance is 60.66%. Figure is taken from reference.¹⁸

The transmittance spectrum of a film dispersed with the three most suitable structures is shown in Figure 6.7, and details of simulating this transmittance is given in the following. According to Beer-Lambert law, transmittance $T(\lambda)$ of incident light of wavelength λ after it travels a distance t in a medium dispersed with nanoparticles is given by:¹⁶

$$T(\lambda) = e^{-N\sigma_{ext}(\lambda)t} \quad (6.4)$$

In Equation (6.4) $\sigma_{ext}(\lambda)$ is the extinction cross section of the dispersed nanoparticle (assuming only one kind of nanoparticle is dispersed) at a wavelength of λ , N is the nanoparticle's volume density. The product of N and t gives areal density N' of the dispersed nanoparticle (the surface of this area is perpendicular to the propagation

direction of incident light), and Equation (6.4) can be written as:

$$T(\lambda) = e^{-N'\sigma_{ext}(\lambda)} \quad (6.5)$$

The area densities of the three most suitable structures are chosen such that transmittance at their corresponding resonance wavelengths become 20%. And this results in an areal density of $1.90 \times 10^9/cm^2$ for red light scatterer (Silica@Au with gain, or item d in Table 6.3), $3.06 \times 10^9/cm^2$ for green light scatterer (Silica@Ag with gain, or item d in Table 6.4) and $4.47 \times 10^9/cm^2$ for blue light scatterer (Ag@Silica with gain, or item b in Table 6.5). And the overall transmittance is the product of the three transmittance spectrums for the three scatterers.

For the discussion up to now, I have assumed constant k over the whole visible wavelength range. But one gain material only provides gain in a small wavelength range, so a negative k over a short wavelength range is more physically meaningful. For this purpose, for the three most suitable structures, I have also investigated the effect on value of FOM when replacing the wavelength-independent k with a gaussian-form k . Here, the gaussian-form k has the following expression:

$$k(\lambda) = k_{optimal} e^{-\frac{(\lambda-\lambda_R)^2}{2a^2}} \quad (6.6)$$

where $k_{optimal}$ and λ_R are the optimized k value and resonance wavelength respectively for a structure with gain material, λ is incident light's wavelength, a is associated with gaussian curve's full width at half maximum (FWHM), and FWHM is assumed to be 30 nm in this section. The gaussian-form k is equal to the optimized k in Tables 6.3, 6.4 and 6.5 at the resonance wavelength, and decreases in magnitude for wavelengths away from the resonance wavelength. For the three most suitable structures, i.e., Silica@Au with gain material (see Table 6.3), Silica@Ag with gain material (see Table 6.4), and Ag@Silica with gain material (see Table 6.5), their values of FOM and their efficiency spectrums calculated with gaussian-form k with other optimized parameters unchanged are shown in Figure 6.8.

Figure 6.8 Efficiency spectrums recalculated for the three most suitable structures, (a) Silica@Au with gain material (corresponding to Figure 6.3 (d)) for red light, (b) Silica@Ag with gain material (corresponding to Figure 6.4 (d)) for green light, and (c) Ag@Silica with gain material (corresponding to Figure 6.5 (b)) for blue light, with gaussian-form k , which is described by equation (6.6).

For the three most suitable structures, as observed from Figure 6.8, after replacing wavelength-independent k with gaussian-form k , change in FOM is not significant. Therefore, this suggests that even when constant k is replaced by gaussian-form k , my conclusion of the three most suitable structures is not affected.

6.4 Conclusion

In this chapter, for the purpose of realizing a transparent projection display, I have searched for structures that may achieve sharp selective scattering of red, green and blue light based on metallic nanoparticle's LSPR effect and gain material's optical compensation. By comparing behaviors of structures optimized with gain material to those without gain material, it is found that for the structures based on Au and Ag, introducing gain material greatly improves the performance in terms of sharper scattering peak and overall lower absorption, while for the Al-based structures little improvement is observed. The most suitable structures for sharp selective scattering of red, green and blue light are respectively found to be Silica@Au, Silica@Ag and Ag@Silica, all with gain material, with their corresponding optimized parameters shown in Tables 6.3, 6.4 and 6.5. A comparison of optimized values of FOM from this chapter with those from previous works reviewed in Section 2.1 and Chapter 4 indicates a great improvement in selective scattering of red, green and blue light with the combination of metallic nanoparticle with gain material. And among gain values of the three most suitable structures, the largest one is still within physical limit.

Chapter 7. Frequency-selective Scattering of Blue and Red Light Based on Silver and Gold Nanocubes

7.1 Introduction

Up to Chapter 6, my research works have been focusing on utilizing spherical core-shell structures to achieve frequency-selective scattering of red, green and blue light, for the purpose of realizing a transparent projection display. However, as reviewed in Section 2.2, non-spherical structures such as Ag ellipsoid, and Ag nanocube can also enable frequency-selective scattering of red, green and blue light.^{14-15 129} Nanospheres and ellipsoids achieve selective scattering of red, green, or blue light by taking advantage of the nanoparticle's dipolar resonance peak,^{13, 15, 97} while Ag nanocubes simultaneously achieve selective scattering of blue and red light by a splitting of resonance peak when it is placed on a dielectric substrate.^{14, 69} For the transparent projection display achieved by depositing Ag nanocubes on TiO₂ thin film reviewed in Section 2.2,¹⁴ it only considers enhancement of backward scattering and its backward scattering of red light is much weaker than that of blue light. So, on top of this, it is of interest to further enhance the backward scattering of red light. As reviewed in Part C of Section 2.2, the resonance peak wavelength of the spectrum of selective backward scattering of blue light (around 460 nm) is quite close to the wavelength of green light (around 530 nm), and the spectrum of the selective backward scattering of blue light has not decreased to zero around the wavelength of green light, which means even when no structure for selective backward scattering of green light is designed, backward scattering of green light still exists (but not as strong as that of blue light). In addition to this, human eyes are sensitive to green light.¹⁶⁵ So for the above two reasons, for the structure of metallic nanocubes on dielectric substrate, it is not intended to enhance backward scattering of green light. Selective backward scattering is useful, because it can be applied to, for example, heads up display (HUD), where navigation or other information is shown on the windshield of a vehicle or of an aircraft. But some

applications find selective forward scattering useful, one example is shop window advertisement where vivid images or movies are displayed on a window wall. For this reason, it is also of interest to determine how to achieve selective forward scattering of blue and red light based on the structure of metallic nanocubes deposited on dielectric substrate. The reason why it is not desired to enhance forward scattering of green light is similar to that for the backward scattering as discussed above. In this chapter, scattering properties of Ag and Au nanocubes deposited on dielectric (TiO_2 or glass) substrate are studied, and three designs for selective scattering of blue and red light are shown, of which, only one is suitable for simultaneous forward and backward selective scattering of blue and red light, the other two are only suitable for either forward or backward selective scattering of blue and red light.

7.2 Simulation details

All simulated results shown in this chapter were calculated by the numerical simulation method known as Finite-Difference Time-Domain (FDTD), as reviewed in Section 3.1. The commercial software to implement FDTD is “FDTD Solutions”. Because the refractive index of TiO_2 is controversial (values between 1.9 to 2.51 have been reported),^{87, 166} I experimentally measured its value. To determine the refractive index of TiO_2 to be used in the simulation, I deposited a layer of TiO_2 thin film with a thickness of 120 nm on a piece of silicon wafer by RF sputtering process followed by calcination at 500°C for 1 h. The refractive index averaged in the visible wavelength range (400–800 nm) of the TiO_2 thin film is 2.3 as obtained with spectroscopic ellipsometry which is reviewed in Section 3.2.⁸⁸ For glass used in subsequent simulations, its refractive index is assumed to be 1.5. In subsequent simulations, for a metallic nanocube placed on dielectric substrate, backscattered light is detected by a box-shaped monitor placed on the same side (with respect to the metallic nanocube) where light is injected (assuming incident light is perpendicular to the air/dielectric interface), whose face nearest and parallel to the air/dielectric interface is open and passes through the geometrical center of the metallic nanocube, while forward scattered

light is collected by another box-shaped monitor placed on the other side, whose open face shares the same plane with that of the back-scattered light monitor. In simulation, the shared open-face of the two box-shaped monitors has a dimension of 400 by 400 nm². The source type is “Total-field scattered-field” (TFSF) so that only the scattered light will be detected by monitors.¹⁶⁷ The grid size of the three-dimensional mesh override region is 1 nm. The edge and corner of a metallic nanocube is rounded by a radius which is 10% of the metallic nanocube’s edge length. The dielectric constants of Ag and Au are taken from reference.³² The fitting of dielectric constants of Ag and Au to experimental data from reference is conducted by the commercial software “FDTD solutions”. The fitted dielectric constants of Ag and Au satisfy Kramers-Kronig relation,¹⁶⁸ and have minimized error with respect to the experimental data from reference.

7.3 Results and Discussion

The resonance peak of a Ag nanocube splits into 2 peaks as the distance between Ag nanocube and a dielectric substrate decreases, and the smaller the distance, the larger the splitting,^{69, 169-173} as shown in Figure 7.1. The mechanism of peak splitting is briefly explained below.

Figure 7.1 FDTD simulation to show when a Ag nanocube (90 nm edge) in air approaches a dielectric substrate (glass), the single scattering peak splits into two. Formation of D and Q modes is explained in text and by Figure 7.3. Figure is adapted from reference.⁶⁹

Embedded in a uniform dielectric medium, a metallic nanocube sustains a dominant bright dipolar plasmon mode and a dominant dark quadrupolar plasmon mode, which are not hybridized to each other. The bright plasmon mode, referred to as the D^0 mode, has its induced charges concentrated on the corners of the cube, with charges of the same sign residing on either side of the cube, as depicted in Figure 7.2 (left). This charge distribution creates a large electric dipole moment and couples strongly to light. The dark plasmon mode, referred to as the Q^0 mode, has its induced charge concentrated on the corners of the cube like D^0 mode but in a manner such that the overall dipole moment disappears, as depicted also in Figure 7.2 (right). This quadrupolar charge distribution cannot couple directly to incident light and the Q^0 mode is therefore dark. The D^0 and Q^0 modes have almost identical charge distribution on the bottom surface of the cube. Therefore, when a dielectric substrate is present, the induced charges in the substrate will mediate an interaction between the D^0 and Q^0 modes, and the two modes will hybridize and form the bonding D and antibonding Q modes, as depicted in Figure 7.3. Thus, the two peaks split from the one resonance peak (corresponding to D^0 mode) after the Ag nanocube is placed on a dielectric substrate correspond to D and Q modes respectively, as shown in Figure 7.1. For more details on the nature of substrate-induced peak splitting of Ag nanocube, readers may refer to the reference from which the above brief explanation is summarized.¹⁶⁹

Figure 7.2 Normalized surface charge distributions for the bright dipolar plasmon mode D^0 (left), and the dark quadrupolar plasmon mode Q^0 (right). Figure is adapted from reference.¹⁶⁹

Figure 7.3 (a) When a Ag nanocube is placed on a dielectric substrate, charges will be induced in the substrate by D^0 and Q^0 modes, and this induced charge mediate D^0 and Q^0 hybridization. (b) An illustration of charge distributions when D^0 and Q^0 modes are fully hybridized, and the forming of the bonding D and antibonding Q modes: $D = D^0 + Q^0$ and $Q = D^0 - Q^0$. (c) Energy diagram demonstrating the effect of dielectric substrate: pure dielectric screening effect (black dashed line) causing red shifts of both D^0 and Q^0 modes and the substrate-mediated hybridization (blue thin line) which leads to the bonding D and antibonding Q modes. Figure is adapted from reference.¹⁶⁹

From my simulation, it is found that the scattering spectrum of a Ag nanocube is affected not only by the presence of dielectric substrate, but also by propagation direction of incident light when the Ag nanocube is placed on a dielectric substrate, as shown in Figure 7.4. As a recap from Section 3.1, the scattering cross section is the ratio of the total scattered power to power flux of the incident light. In Figure 7.4, a splitting of scattering peak is observed when the Ag nanocube in air is placed on TiO_2 substrate, and the scattering peak around 440 nm is stronger than that around 710 nm

when light is incident from air to TiO_2 substrate (Air-to- TiO_2 in short), and the other way around when light is incident from TiO_2 substrate to air (TiO_2 -to-Air in short).

Figure 7.4 Scattering cross sections (in nm^2) calculated for Ag nanocube with edge length of 100 nm in three setups: without dielectric substrate (solid red line), with TiO_2 substrate and light incident from air to TiO_2 (dashed green line), with TiO_2 substrate and light incident from TiO_2 to air (dashed blue line). Insets illustrate the propagation direction and polarization of light. Figure is taken from reference.¹⁷⁴

In this chapter, forward scattering cross section refers to the integral of the differential scattering cross section over the forward hemisphere (i.e., integral of all scattered light with scattering angle between 0° to 90°), and backward scattering cross section refers to the integral of the differential scattering cross section over the backward hemisphere (i.e., integral of all scattered light with scattering angle between 90° to 180°).

The Air-to- TiO_2 and TiO_2 -to-Air scattering spectrums for Ag nanocube placed on TiO_2 substrate as shown in Figure 7.4 are further decomposed into forward and backward scattering, respectively illustrated in Figure 7.5(a) and Figure 7.6(a). It is observed that

the forward scatterings are quite different from the backward scatterings. For the two peaks of the Air-to-TiO₂ scattering as shown in Figure 7.4, their near electric field amplitude $|E|$ spatial plots are shown in Figures 7.2(b) and 7.2(c) respectively, while for the two peaks of the TiO₂-to-Air scattering, their $|E|$ spatial plots are shown in Figures 7.3(b) and 7.3(c), respectively. In Figures 7.2 and 7.3, by correlating peaks of forward and backward scattering spectrums to respective near field plots, an interesting finding is described in the following. When the end of the nanocube with higher $|E|$, which is the active region of free electrons' resonant oscillation, is nearer to the incident light source (as compared to the other end of the nanocube with lower $|E|$), backward scattering dominates around the peak wavelength; and in the reverse case, i.e., when the end of the nanocube with higher $|E|$ is away from the incident light source, forward scattering dominates around the peak wavelength.

Figure 7.5 (a) Forward and backward components of scattering cross section of 100-nm Ag nanocube placed on TiO_2 substrate, with the light propagation direction (Air-to- TiO_2) and polarization illustrated by the inset. (b) Near electric field amplitude $|E|$ spatial plot at Peak I (wavelength = 435 nm) as indicated in (a). (c) Near electric field amplitude $|E|$ spatial plot at Peak II (wavelength = 710 nm) as indicated in (a). The white dotted line in (b) and (c) indicates the Air/ TiO_2 interface. The plane at which amplitude of electric field is recorded is parallel to paper and is placed 1 nm away from the front face of Ag nanocube. Figure is taken from reference.¹⁷⁴

Figure 7.6 (a) Forward and backward components of scattering cross section of 100-nm Ag nanocube placed on TiO_2 substrate, with light propagation direction (TiO_2 -to-Air) and polarization illustrated by the inset. (b) Near electric field amplitude $|E|$ spatial plot at Peak I (wavelength = 440 nm) as indicated in (a). (c) Near electric field amplitude $|E|$ spatial plot at Peak II (wavelength = 710 nm) as indicated in (a). The white dotted line in (b) and (c) indicates the Air/ TiO_2 interface. The plane at which amplitude of electric field is recorded is parallel to paper and is placed 1 nm away from the front face of Ag nanocube. Figure is taken from reference.¹⁷⁴

Therefore, from Figures 7.2 and 7.3, for backward scattering, the Air-to- TiO_2 setup may offer a solution for blue light (wavelength of about 440 to 460 nm) selective scattering while the TiO_2 -to-Air setup may provide a solution for red light (wavelength of about 620 to 700 nm) selective scattering. In terms of forward scattering, for both setups of Air-to- TiO_2 and TiO_2 -to-Air, differences between red light and blue light scattering magnitudes are not significant, so both setups of Air-to- TiO_2 and TiO_2 -to-Air may achieve simultaneous selective scattering of blue and red light. As reviewed in Chapter

2, metallic nanoparticle's resonance peak positions as well as magnitude of light scattering are also affected by metallic nanoparticle's size.¹⁶⁻¹⁷ With the above considerations, forward (Figures 7.4(a) and 7.4(b)) and backward (Figures 7.5(a) and 7.5(b)) scattering cross sections are calculated for TiO₂ substrate/Ag nanocubes of several sizes (edge length = 90, 100, 110, 120, and 130 nm), for both setups of Air-to-TiO₂ and TiO₂-to-Air, to search for the best solutions for selective scattering of blue and red light.

Figure 7.7 Simulated forward scattering cross sections for TiO₂-substrate/Ag nanocubes are shown in (a) and (b), and for glass-substrate/Au nanocubes are shown in (c) and (d). Incident direction and polarization of light for each sub-figure are illustrated by its corresponding inset. Figure legends denote the edge lengths of nanocubes. For all simulations shown in this figure, a 2-nm gap between the bottom of nanocube and the dielectric substrate is assumed to simulate the protective reagent in a real situation,¹⁴ such as PVP (Polyvinyl Pyrrolidone). The scale of the vertical axis is the same for all sub-figures for easy comparison. Figure is taken from reference.¹⁷⁴

Figure 7.8 Simulated backward scattering cross sections for TiO₂-substrate/Ag nanocubes are shown in (a) and (b), and for glass-substrate/Au nanocubes are shown in (c) and (d). Incident direction and polarization of light for each sub-figure are illustrated by its corresponding inset. Figure legends denote the edge lengths of nanocubes. For all simulations shown in this figure, a 2-nm gap between the bottom of nanocube and the dielectric substrate is assumed to simulate the protective reagent in a real situation,¹⁴ such as PVP (Polyvinyl Pyrrolidone). The scale of the vertical axis is the same for all sub-figures for easy comparison. Figure is taken from reference.¹⁷⁴

From Figures 7.4(a) and 7.4(b) and Figures 7.5(a) and 7.5(b), it is observed that the scattering peaks intended for red light selective scattering at longer wavelengths are broader than those intended for blue light selective scattering at shorter wavelengths, but narrow scattering peak width is more desirable. To search for red light scattering peak with narrow width, forward (Figures 7.4(c) and 7.4(d)) and backward (Figures 7.5(c) and 7.5(d)) scattering cross sections are calculated for glass substrate/Au nanocubes of several sizes (edge length = 100, 110, 120, 130, and 140 nm), for both

setups of Air-to-Glass (light is incident from air to glass) and Glass-to-Air (light is incident from glass to air). The reason to investigate scattering properties of Au nanocubes is that Au has a high quality factor (defined by $-\varepsilon_1(\omega)/\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of metal's dielectric function, respectively, and the higher this value, the stronger the resonance strength) around the wavelength range of red light,⁸⁵ which suggests Au nanocubes may generate sharp and strong scattering peaks for red light. The reason for choosing glass rather than TiO₂ as the dielectric substrate for Au nanocubes is given as follows. The simulation results obtained with TiO₂-substrate (shown in the Figure 7.9) suggest that due to TiO₂'s high refractive index, there is a trade-off between resonance peak wavelength and magnitude of scattering, i.e., when increasing Au nanocube's size to increase magnitude of scattering cross section to a desirable value, the resonance peak wavelength is undesirably redshifted beyond 700 nm at the meantime.

Figure 7.9 Calculated scattering cross sections of TiO₂ substrate/Au nanocube of different sizes. (a) Light is incident from air to TiO₂, and (b) light is incident from TiO₂ to air. Insets show the schematics for the two setups. Legends indicate the edge lengths of Au nanocubes. It is observed that when resonance peak wavelengths are smaller than 700 nm, scattering cross sections of TiO₂ substrate/Au nanocubes are smaller than $5 \times 10^4 \text{ nm}^2$, which is too small compared to those of glass substrate/Au nanocubes, but by increasing Au nanocube's size to increase its scattering cross section, its peak wavelength is beyond 700 nm, for both setups of Air-to-TiO₂ and TiO₂-to-Air as shown in (a) and (b). And forward and backward scattering cross sections are even smaller when resonance peak wavelength is smaller than 700 nm, since scattering cross section is the sum of these two. Figure is taken from reference.¹⁷⁴

A suitable scattering peak for selective scattering of blue or red light should satisfy two criteria: first, the magnitude of scattering cross section around the peak wavelength

should be as large as possible, because for transparent projection display based on the dielectric substrate/metallic nanocubes structure, only one layer of metallic nanocubes can be deposited; second, the peak wavelength should be within the desirable wavelength ranges, i.e., for blue light scattering, the peak wavelength should be within the range of 440–460 nm, and for red light scattering, the peak wavelength should be within 620–700 nm. Therefore, according to these criteria and based on the observations from Figs. 4 and 5, suitable setups for selective scattering of blue and red light can be summarized as:

1. Forward scattering of blue light: 120 nm Ag nanocube with TiO₂-to-Air (Figure 7.7(b) blue curve).
2. Forward scattering of red light: 120 nm Ag nanocube with Air-to-TiO₂ (Figure 7.7(a) blue curve), and 130-nm Au nanocube with Air-to-Glass (Figure 7.7(c) blue curve).
3. Backward scattering of blue light: 120 nm Ag nanocube with Air-to-TiO₂ (Figure 7.8(a) blue curve).
4. Backward scattering of red light: 120 nm Ag nanocube with TiO₂-to-Air (Figure 7.8(b) blue curve), and 130-nm Au nanocube with Glass-to-Air (Figure 7.8(d) blue curve).

Therefore, the following two combinations can achieve forward simultaneous selective scattering of blue and red light: 120 nm Ag nanocube with TiO₂-to-Air (Figure 7.7(b)) blue curve) + 120 nm Ag nanocube with Air-to-TiO₂ (Figure 7.7(a) blue curve), and 120 nm Ag nanocube with TiO₂-to-Air (Figure 7.7(b) blue curve) + 130 nm Au nanocube with Air-to-Glass (Figure 7.7(c) blue curve). Similarly, to achieve backward simultaneous selective scattering of blue and red light, there are also two combinations: 120 nm Ag nanocube with Air-to-TiO₂ (Figure 7.8(a) blue curve)+120-nm Ag nanocube with TiO₂-to-Air (Figure 7.8(b) blue curve), and 120 nm Ag nanocube with Air-to-TiO₂ (Figure 7.8(a) blue curve)+130-nm Au nanocube with Glass-to-Air (Figure 7.8(d) blue curve). Note that the combination (120-nm Ag nanocube with Air-to-TiO₂)

+ (120 nm Ag nanocube with TiO₂-to-Air) appears both in forward and backward scattering, which indicates that this combination can achieve both forward and backward selective scattering of blue and red light. Therefore, there are only three combinations for simultaneous scattering of blue and red light:

1. Forward scattering: (120 nm Ag nanocube with TiO₂-to-Air) + (130 nm Au nanocube with Air-to-Glass)
2. Backward scattering: (120 nm Ag nanocube with Air-to-TiO₂) + (130 nm Au nanocube with Glass-to-Air)
3. Forward and backward scattering: (120 nm Ag nanocube with Air-to-TiO₂) + (120 nm Ag nanocube with TiO₂-to-Air)

The schematics of the three combinations are shown in insets of Figure 7.10, with TiO₂ as coating layer(s) on glass, and glass as the substrate. The interface between two different media reflects light, thus the amount of light reaching the back side (as opposed to the side where incident light is injected) of the TiO₂-coated glass slip is reduced, which decreases scattering of metallic nanocubes placed on this side. Therefore, it is important to reduce light reflection by properly selecting thickness of TiO₂ layer(s) coated on glass. For the first combination, it is desirable to reduce reflection of red light because Au nanocube placed on the back side is responsible for red light backward scattering. Reduction of red-light reflection can be achieved by a destructive interference between the light reflected at the air/TiO₂ interface and the light reflected at the TiO₂/glass interface. Light reflection at the air/TiO₂ interface has a phase-shift of 180°, while light reflection at the TiO₂/glass (TiO₂/air) has no phase-shift, so a destructive interference between these two reflections is realized by choosing the TiO₂ thin film's thickness to be $\lambda_{red}/(2n)$, where λ_{red} is the red light's wavelength in vacuum and is chosen to be 650 nm in our work, and n is the refractive index of the TiO₂ thin film which is measured to be 2.3. Thus, thickness of the TiO₂ thin film for the first combination is decided to be 137 nm. Similarly, for the second combination, since Ag nanocube placed on the back side is responsible for blue light forward scattering,

reduction of blue-light reflection is desired and thickness of the TiO_2 thin film of this combination is decided to be 100 nm. For the third combination, Ag nanocube placed on the back side is responsible for both blue and red light scattering, so to achieve a balance, the wavelength at which the light's reflection to be minimized is selected to be 550 nm, leading to a thickness of 120 nm for TiO_2 thin film of this combination.

For the first combination, backward scattering from Ag nanocube is combined with that from Au nanocube, with consideration of TiO_2 thin film's thickness and light reflections at all interfaces, and is shown as an overall backward scattering in Figure 7.10(a). Similarly, combined overall forward scattering for the second combination is shown in Figure 7.10(b), and both combined overall forward and backward scattering spectrums for the third combination are shown in Figure 7.10(c).

Figure 7.10 Combined overall forward or backward scattering cross sections for the three combinations discussed in text, with their schematics shown by insets, and effect of TiO₂ thin film's thickness and light reflections at all interfaces are considered for all three combinations. (a) Overall backward scattering for the first combination combined from those of Ag nanocube and Au nanocube, thickness of the TiO₂ thin film is 137 nm. (b) Overall forward scattering for the second combination combined from those of Ag nanocube and Au nanocube, thickness of the TiO₂ thin film is 100 nm. (c) Overall forward scattering as well as backward scattering for the third combination combined from that of Ag nanocube at the foreside and that of Ag nanocube at the back side, thickness of both the two TiO₂ thin films is 120 nm. In (a), (b) and (c), Ag nanocube's edge length is 120 nm. In (a) and (b), Au nanocube's edge length is 130 nm. For all simulations shown in this figure, a 2-nm gap between the bottom of nanocube and the dielectric substrate is assumed to simulate protective reagent in a real situation,¹⁴ such as PVP (Polyvinyl Pyrrolidone). Figure is taken from reference.¹⁷⁴

From Figure 7.10, it is observed that all three combinations achieve selective

enhancement of blue and red light scattering, either in forward or backward or both directions. And given a scattering cross section of about 50000 nm^2 at peak wavelength for a single nanoparticle is able to generate a clear projected image with proper areal nanoparticle density as demonstrated in previous work,¹⁴ all three combinations as shown in Figure 7.10 have enough magnitudes of scattering and are expected to generate clear projected image with suitable areal concentration of nanocubes. In Figure 7.10(b), the relative weaker peak around 455 nm for blue light forward scattering can be strengthened by increasing areal concentration of Ag nanocubes deposited on the back side of the TiO_2 -coated glass slide relative to that of Au nanocubes deposited on the foreside in a real application. For each combination shown in Figure 7.10, angular distribution of scattering is plotted for both peaks and shown in Figure 7.11. In practice, the surface of TiO_2 thin film coated on the glass is not perfectly smooth, in other words, there must be some surface roughness. Surface roughness effectively approximates a thin layer with lower refractive index on the TiO_2 thin film and is equivalent to a distance between Ag nanocube and TiO_2 . Therefore, referring to the trend shown in Figure 7.1, surface roughness decreases the degree of peak splitting. To compensate for the effect of surface roughness, one can try to reduce surface roughness by polishing process, or by increasing the refractive index of TiO_2 film by changing it to rutile phase.¹⁷⁵ Since it is also reported when a Ag nanocube is placed on a dielectric substrate, the larger the substrate's refractive index, the larger the peak splitting effect.^{69, 169}

Figure 7.11 Normalized scattering intensity $|E|^2$ plotted versus scattering angle for the three combinations shown in Figure 7.10. (a) Plotting for the first combination at the wavelength of 455 nm. (b) Plotting for the first combination at the wavelength of 680 nm. (c) Plotting for the second combination at the wavelength of 460 nm. (d) Plotting for the second combination at the wavelength of 680 nm. (e) Plotting for the third combination at the wavelength of 460 nm. (f) Plotting for the third combination at the wavelength of 685 nm. All scattering intensities shown in this figure consist of contributions from both the nanocubes placed on the foreside and backside of the TiO_2 -coated glass slide. Incident light has equal components for s- and p- polarisations with respect to the scattering plane. Each sub-figure's angular distribution of scattering intensity is normalized to its largest value. Figure is taken from reference.¹⁷⁴

From Figure 7.11, it is observed that the angular distribution of scattering is relatively isotropic for both peaks in backward direction (90° to 180°) for the first combination, in forward direction (0° to 90°) for the second combination, and in both forward and backward directions (0° to 180°) for the third combination. These indicate projected image can be viewed clearly within a reasonable angle range (refer to the polar plots in Figure 7.11 for angles stated here): about 135° to 180° for the combinations suitable

for backward scattering (combinations 1 and 3), and about 0° to 50° for the combinations suitable for forward scattering (combinations 2 and 3).

7.4 Conclusion

In this chapter, through numerical simulations, forward and backward scattering properties of Ag and Au nanocubes placed on dielectric substrate are investigated, with effect of nanocube's size and both setups of Air-to-Dielectric (light is incident from air to dielectric) and Dielectric-to-Air (light is incident from dielectric to air) taken into account. Based on the forward and backward scattering properties, three designs (the three combinations shown in Figure 7.10) are proposed, two of which achieve selective scattering of blue and red light only in either forward or backward direction, and the other one achieves selective scattering of blue and red light both in forward and backward directions, all with reasonable large magnitudes of scattering strength. Simulated angular distribution of scattering suggests that the viewing-angle range is large for all the three designs.

Chapter 8. Conclusion and Recommendations

8.1 Conclusion

Transparent display has many applications and many solutions have been proposed for it. One approach to achieve transparent projection display is that such a transparent projection display only selectively scatters red, green and blue light and transmits visible light of other colours. One way to achieve frequency-selective scattering of light is to take advantage of metallic nanoparticle's localized surface plasmon resonance (LSPR).

Through the literature review in Chapter 2, it is known that metallic nanoparticle's LSPR peak is affected by many factors: the constituent material, size of the nanoparticle, refractive index of the surrounding medium, nanoparticle's shape. Thus, these factors indicate that engineering a metallic nanoparticle's LSPR peak and thus frequency-selective light scattering properties is possible. And before the commencement of this thesis' research works, existing researches exploring metallic nanoparticle's LSPR properties for the purpose of transparent projection display are reviewed in Chapter 2, demonstrating that Ag is the most suitable nanoparticle's constituent material to generate nanostructures with high frequency-selectivity of light scattering in visible wavelength region, and that frequency-selective scattering can be achieved by the following structures: spherical Silica core with spherical Ag shell, Ag ellipsoid and Ag nanocube.

In Chapter 3, methods for simulating nanoparticle's light scattering and absorption properties are reviewed. The Mie theory, an exact solution of Maxwell's equations, is suitable for simulating the following structures: sphere, coated sphere, infinite cylinder, and spheroid. For arbitrarily shaped nanoparticle, numerical methods have to be used, a typical one is the Finite Difference Time Domain (FDTD) method. Apart from

simulation methods, Spectroscopic Ellipsometry (SE), a method for measuring material's dielectric function, is also briefly reviewed.

The reported nano-structures in Chapter 2 only experimentally realized frequency-selective scattering of blue light, although theoretical structures for green and red light are also proposed. So, in Chapter 4, I proposed the structure of Ag@TiO₂ (spherical Ag core coated with spherical TiO₂ shell), from which, a transparent projection display that selectively scatters green light is experimentally realized. But, as with the nanoparticles reviewed in Chapter 2, the light scattering's frequency-selectivity of Ag@TiO₂ is far from the ideal case as shown in Figure 1.1, namely, the light scattering peak is not narrow enough, and the light absorption level is not low enough.

In Chapter 5, size effect on metallic nanoparticle's light scattering and absorption properties is investigated. The size of a metallic nanoparticle is usually smaller than or comparable to electrons' mean free path in the constituent metal's bulk form, therefore electrons in metallic nanoparticle go through more collisions per unit time than they do in bulk metal. Through simulation studies and experimental verifications on Au nanoshell (i.e., spherical Silica core coated with spherical Au shell), this phenomenon, referred to as surface scattering of free (or conduction) electrons, is shown to broaden light scattering peak width (and therefore decrease frequency-selectivity of light scattering), decrease light scattering strength and increase light absorption strength. Therefore, surface scattering of free electrons undesirably degenerates metallic nanoparticle's performance of light scattering in a transparent projection display.

Despite performances of Ag@TiO₂ studied in Chapter 4, Silica@Ag, Ag ellipsoid and Ag nanocube reviewed in Chapter 2 are far inferior to the ideal case shown in Figure 1.1, a remedy is proposed in Chapter 6 which has the potential to generate sharp frequency-selective light scattering peak(s): combining metallic nanoparticles with gain material. Three structures, Silica@Au, Silica@Ag and Ag@Silica, whose Silica are

doped with gain material, are proposed which generate sharp frequency-selective light scattering peaks around red, green and blue light, respectively, with low level of light absorption.

Up to Chapter 6, I have only studied light scattering and absorption properties of spherical nanoparticles. In Chapter 7 scattering properties of Ag and Au nanocube deposited on dielectric (TiO_2 or glass) substrate are studied, and three designs for selective scattering of blue and red light are shown, of which, only one is suitable for simultaneous forward and backward selective scattering of blue and red light, the other two are only suitable for either forward or backward selective scattering of blue and red light.

8.2 Recommendations

Efforts presented in this thesis are targeted to realize sharp frequency-selective scattering of red, green and blue light, for the purpose of achieving transparent projection display. However, it is still far away from the target. Therefore, several future works are recommended.

Firstly, for the idea of combining gain material with metallic nanoparticle, and the structures proposed in Chapter 6, experimental realization of them is worth trying.

Secondly, for the structure of metallic nanoparticle placed on dielectric substrate, light scattering and absorption properties have only been studied for the shape of nanocube. Therefore, it is recommended that studies on other shapes, such as nano-star, nano-triangle and nano-rice may be attempted. And, it is also interesting to investigate how it will affect their light scattering and absorption properties by coating these nanoparticles with a thin layer of dielectric doped with gain material.

Lastly, doped dielectric nanoparticles may be a promising way of achieving frequency-

selective scattering of light, as they do not suffer from light absorption as compared to metallic nanoparticle. One example is shown in supplementary material of reference.¹³

List of Publications

Journals:

- [1] **Y. Ye**, T. Chen, J. Zhen, C. Xu, J. Zhang, and H. Li, "Resonant scattering of green light enabled by Ag@TiO₂ and its application in a green light projection screen," *Nanoscale*, vol. 10, pp. 2438-2446, 2018.
- [2] **Y. Ye**, T. P. Chen, Z. Liu, and X. Yuan, "Effect of Surface Scattering of Electrons on Ratios of Optical Absorption and Scattering to Extinction of Gold Nanoshell," *Nanoscale research letters*, vol. 13, pp. 299-299, 2018.
- [3] **Y. Ye**, R. Liu, Z. Song, Z. Liu, and T. P. Chen, "Sharp selective scattering of red, green, and blue light achieved via gain material's loss compensation," *Optics Express*, vol. 27, pp. 9189-9204, 2019.
- [4] **Y. Ye** and T. P. Chen, "Selective Scattering of Blue and Red Light Based on Silver and Gold Nanocubes," *ECS Journal of Solid State Science and Technology*, vol. 8, pp. R51-R57, January 1, 2019.
- [5] **Ye Y Y**, Liu Z, Chen T P, "Toward transparent projection display: recent progress in frequency-selective scattering of RGB light based on metallic nanoparticle's localized surface plasmon resonance," *Opto-Electron Adv* 2, 190020, 2019.

Conference:

- [1] **Yiyang Ye**, T. P. Chen, Huakai Li, Chen Xu, Jun Zhang, and Jianxun Sun, "Modelling of the Size Limitation of Silver Nanowires Used as Transparent Conductor to Achieve Balance between Optical Transmittance and Electrical Conductivity," *International Conference on Materials for Advanced Technologies*, Singapore, June 2017.

As Contributing Author:

- [1] J. Xiong, S. Li, Y. Ye, J. Wang, K. Qian, P. Cui, D. Gao, M.-F. Lin, T. P. Chen, and P. S. Lee, "A Deformable and Highly Robust Ethyl Cellulose Transparent Conductor with a Scalable Silver Nanowires Bundle Micromesh," *Advanced Materials*, 30 (36), 1802803, 2018.

Bibliography

1. Head-up Display Market. <https://www.marketsandmarkets.com/PressReleases/head-up-display.asp> (accessed 8th April 2019).
2. End of Year Summary of Augmented Reality and Virtual Reality Market Size Predictions. <https://medium.com/vr-first/a-summary-of-augmented-reality-and-virtual-reality-market-size-predictions-4b51ea5e2509> (accessed 8th April 2019).
3. Liu, S.; Yuan, F.; Chen, A.; Zhang, H.; Chang, S.; Liu, J.; Zhu, L.; Zheng, Z., *Color Transparent Screen Using Planar Glass Combined with Lens Array Holographic Optical Elements*; SPIE, 2016; Vol. 9948.
4. Li, G.; Lee, D.; Jeong, Y.; Cho, J.; Lee, B., Holographic Display for See-through Augmented Reality Using Mirror-Lens Holographic Optical Element. *Opt. Lett.* **2016**, *41*, 2486-2489.
5. Newman, R. L., *Head-up Displays: Designing the Way Ahead*; Routledge, 2017.
6. Goldenberg, J. F.; McKechnie, T. S., Diffraction Analysis of Bulk Diffusers for Projection-Screen Applications. *J. Opt. Soc. Am. A* **1985**, *2*, 2337-2347.
7. Diebold, M. P., *Application of Light Scattering to Coatings: A User's Guide*; Springer, 2014.
8. Sun, T.; Pettitt, G.; Ho, N. T.; Eckles, K.; Clifton, B.; Cheng, B., *Full Color High Contrast Front Projection on Black Emissive Display*, SPIE, 2012; Vol. 8254.
9. Geffroy, B.; le Roy, P.; Prat, C., Organic Light-Emitting Diode (Oled) Technology: Materials, Devices and Display Technologies. *Polymer International* **2006**, *55*, 572-582.
10. Urabe, T.; Sasaoka, T.; Tatsuki, K.; Takaki, J., 13.1: Invited Paper: Technological Evolution for Large Screen Size Active Matrix Oled Display. *SID Symposium Digest of Technical Papers* **2007**, *38*, 161-164.
11. Pardo, D. A.; Jabbour, G. E.; Peyghambarian, N., Application of Screen Printing in the Fabrication of Organic Light-Emitting Devices. *Advanced Materials* **2000**, *12*, 1249-1252.
12. Park, J.-S.; Chae, H.; Chung, H. K.; Lee, S. I., Thin Film Encapsulation for Flexible Am-Oled: A Review. *Semiconductor science and technology* **2011**, *26*, 034001.
13. Hsu, C. W.; Zhen, B.; Qiu, W.; Shapira, O.; DeLacy, B. G.; Joannopoulos, J. D.; Soljačić, M., Transparent Displays Enabled by Resonant Nanoparticle Scattering. *Nature Communications* **2014**, *5*, 3152.
14. Saito, K.; Tatsuma, T., A Transparent Projection Screen Based on Plasmonic Ag Nanocubes. *Nanoscale* **2015**, *7*, 20365-20368.
15. Monti, A.; Toscano, A.; Bilotti, F., Analysis of the Scattering and Absorption Properties of Ellipsoidal Nanoparticle Arrays for the Design of Full-Color Transparent Screens. *Journal of Applied Physics* **2017**, *121*, 243106.
16. Kreibig, U.; Vollmer, M., *Optical Properties of Metal Clusters*; Springer Science & Business Media, 2013.
17. Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C., The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *The Journal of Physical Chemistry B* **2003**, *107*, 668-677.
18. Ye, Y.; Liu, R.; Song, Z.; Liu, Z.; Chen, T. P., Sharp Selective Scattering of Red, Green, and Blue Light Achieved Via Gain Material’S Loss Compensation. *Opt. Express* **2019**, *27*, 9189-9204.
19. Agrawal, A.; Cho, S. H.; Zandi, O.; Ghosh, S.; Johns, R. W.; Milliron, D. J., Localized Surface

- Plasmon Resonance in Semiconductor Nanocrystals. *Chemical Reviews* **2018**, *118*, 3121-3207.
20. Zhou, S.; Pi, X.; Ni, Z.; Ding, Y.; Jiang, Y.; Jin, C.; Delerue, C.; Yang, D.; Nozaki, T., Comparative Study on the Localized Surface Plasmon Resonance of Boron- and Phosphorus-Doped Silicon Nanocrystals. *ACS Nano* **2015**, *9*, 378-386.
 21. Zhu, Z., et al., Near-Infrared Plasmonic 2d Semimetals for Applications in Communication and Biology. *Advanced Functional Materials* **2016**, *26*, 1793-1802.
 22. Li, J.; Cushing, S. K.; Meng, F.; Senty, T. R.; Bristow, A. D.; Wu, N., Plasmon-Induced Resonance Energy Transfer for Solar Energy Conversion. *Nature Photonics* **2015**, *9*, 601.
 23. Hollstein, T.; Kreibig, U.; Leis, F., Optical Properties of Cu and Ag in the Intermediate Region between Pure Drude and Interband Absorption. *physica status solidi (b)* **1977**, *82*, 545-556.
 24. Kreibig, U., The Transition Cluster-Solid State in Small Gold Particles. *Solid State Communications* **1978**, *28*, 767-769.
 25. Bohren, C. F.; Huffman, D. R., *Absorption and Scattering of Light by Small Particles*; John Wiley & Sons, 2008.
 26. Underwood, S.; Mulvaney, P., Effect of the Solution Refractive Index on the Color of Gold Colloids. *Langmuir* **1994**, *10*, 3427-3430.
 27. Mulvaney, P., Surface Plasmon Spectroscopy of Nanosized Metal Particles. *Langmuir* **1996**, *12*, 788-800.
 28. Barber, P. W.; Chang, R. K., *Optical Effects Associated with Small Particles*; World Scientific, 1988; Vol. 1.
 29. D'Elia, S.; Scaramuzza, N.; Ciuchi, F.; Versace, C.; Strangi, G.; Bartolino, R., Ellipsometry Investigation of the Effects of Annealing Temperature on the Optical Properties of Indium Tin Oxide Thin Films Studied by Drude-Lorentz Model. *Applied Surface Science* **2009**, *255*, 7203-7211.
 30. Quinten, M., *Optical Properties of Nanoparticle Systems: Mie and Beyond*; John Wiley & Sons, 2010.
 31. Kreibig, U., Small Silver Particles in Photosensitive Glass: Their Nucleation and Growth. *Applied physics* **1976**, *10*, 255-264.
 32. Palik, E. D., *Handbook of Optical Constants of Solids*; Academic press, 1998; Vol. 3.
 33. Draine, B. T.; Flatau, P. J., Discrete-Dipole Approximation for Scattering Calculations. *JOSA A* **1994**, *11*, 1491-1499.
 34. Wriedt, T., Using the T-Matrix Method for Light Scattering Computations by Non-Axisymmetric Particles: Superellipsoids and Realistically Shaped Particles. *Particle & Particle Systems Characterization* **2002**, *19*, 256-268.
 35. Jain, P. K.; Lee, K. S.; El-Sayed, I. H.; El-Sayed, M. A., Calculated Absorption and Scattering Properties of Gold Nanoparticles of Different Size, Shape, and Composition: Applications in Biological Imaging and Biomedicine. *The Journal of Physical Chemistry B* **2006**, *110*, 7238-7248.
 36. and, S. L.; El-Sayed, M. A., Optical Properties and Ultrafast Dynamics of Metallic Nanocrystals. *Annual Review of Physical Chemistry* **2003**, *54*, 331-366.
 37. van der Zande, B. M. I.; Böhmer, M. R.; Fokkink, L. G. J.; Schönenberger, C., Aqueous Gold Sols of Rod-Shaped Particles. *The Journal of Physical Chemistry B* **1997**, *101*, 852-854.
 38. Saito, K.; Tatsuma, T., Asymmetric Three-Way Plasmonic Color Routers. *Advanced Optical Materials* **2015**, *3*, 883-887.
 39. Tsung, C.-K.; Hong, W. B.; Shi, Q. H.; Kou, X. S.; Yeung, M. H.; Wang, J. F.; Stucky, G. D., Shape- and Orientation-Controlled Gold Nanoparticles Formed within Mesoporous Silica Nanofibers.

Advanced Functional Materials **2006**, *16*, 2225-2230.

40. An, L.; Wang, Y.; Tian, Q.; Yang, S., Small Gold Nanorods: Recent Advances in Synthesis, Biological Imaging, and Cancer Therapy. *Materials* **2017**, *10*, 1372.
41. Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G., Photoinduced Conversion of Silver Nanospheres to Nanoprisms. *Science* **2001**, *294*, 1901-1903.
42. El-Sayed, M. A., Some Interesting Properties of Metals Confined in Time and Nanometer Space of Different Shapes. *Accounts of Chemical Research* **2001**, *34*, 257-264.
43. Napper, D. H., A Diffraction Theory Approach to the Total Scattering by Cubes. *Kolloid-Zeitschrift und Zeitschrift für Polymere* **1967**, *218*, 41-46.
44. Fuchs, R., Theory of the Optical Properties of Ionic Crystal Cubes. *Physical Review B* **1975**, *11*, 1732-1740.
45. Bergman, D. J., The Dielectric Constant of a Composite Material—a Problem in Classical Physics. *Physics Reports* **1978**, *43*, 377-407.
46. Stroud, D., The Effective Medium Approximations: Some Recent Developments. *Superlattices and Microstructures* **1998**, *23*, 567-573.
47. Garnett, J. M., Xii. Colours in Metal Glasses and in Metallic Films. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character* **1904**, *203*, 385-420.
48. Aden, A. L.; Kerker, M., Scattering of Electromagnetic Waves from Two Concentric Spheres. *Journal of Applied Physics* **1951**, *22*, 1242-1246.
49. Qiu, W.; DeLacy, B. G.; Johnson, S. G.; Joannopoulos, J. D.; Soljačić, M., Optimization of Broadband Optical Response of Multilayer Nanospheres. *Opt. Express* **2012**, *20*, 18494-18504.
50. Sinzig, J.; Quinten, M., Scattering and Absorption by Spherical Multilayer Particles. *Applied Physics A* **1994**, *58*, 157-162.
51. Chen, Y.-S.; Frey, W.; Kim, S.; Kruizinga, P.; Homan, K.; Emelianov, S., Silica-Coated Gold Nanorods as Photoacoustic Signal Nanoamplifiers. *Nano Letters* **2011**, *11*, 348-354.
52. Loo, C.; Lin, A.; Hirsch, L.; Lee, M.-H.; Barton, J.; Halas, N.; West, J.; Drezek, R., Nanoshell-Enabled Photonics-Based Imaging and Therapy of Cancer. *Technology in Cancer Research & Treatment* **2004**, *3*, 33-40.
53. Oraevsky, A. A.; Karabutov, A. A.; Savateeva, E. V., *Enhancement of Optoacoustic Tissue Contrast with Absorbing Nanoparticles*, SPIE, 2001; Vol. 4434.
54. Agarwal, A.; Huang, S. W.; O'Donnell, M.; Day, K. C.; Day, M.; Kotov, N.; Ashkenazi, S., Targeted Gold Nanorod Contrast Agent for Prostate Cancer Detection by Photoacoustic Imaging. *Journal of Applied Physics* **2007**, *102*, 064701.
55. Otto, A., Surface-Enhanced Raman Scattering of Adsorbates. *Journal of Raman Spectroscopy* **1991**, *22*, 743-752.
56. Otto, A.; Mrozek, I.; Grabhorn, H.; Akemann, W., Surface-Enhanced Raman Scattering. *Journal of Physics: Condensed Matter* **1992**, *4*, 1143.
57. Bohren, C. F.; Clothiaux, E. E., Fundamentals of Atmospheric Radiation - an Introduction with 400 Problems. *Fundamentals of Atmospheric Radiation - An Introduction with 400 Problems* **2006**.
58. Yang, W., Improved Recursive Algorithm for Light Scattering by a Multilayered Sphere. *Appl. Opt.* **2003**, *42*, 1710-1720.
59. Kucherenko, S.; Sytsko, Y., Application of Deterministic Low-Discrepancy Sequences in Global Optimization. *Computational Optimization and Applications* **2005**, *30*, 297-318.

60. Johnson, S. G. The Nlopt Nonlinear-Optimization Package. <https://nlopt.readthedocs.io/en/latest/> (accessed 23rd March 2019).
61. Ye, Y.; Chen, T. P.; Liu, Z.; Yuan, X., Effect of Surface Scattering of Electrons on Ratios of Optical Absorption and Scattering to Extinction of Gold Nanoshell. *Nanoscale research letters* **2018**, *13*, 299-299.
62. Kreibig, U.; Fragstein, C. v., The Limitation of Electron Mean Free Path in Small Silver Particles. *Zeitschrift für Physik* **1969**, *224*, 307-323.
63. Tang, S.; Tang, Y.; Zhu, S.; Lu, H.; Meng, X., Synthesis and Characterization of Silica–Silver Core–Shell Composite Particles with Uniform Thin Silver Layers. *Journal of Solid State Chemistry* **2007**, *180*, 2871-2876.
64. Fruhnert, M.; Monti, A.; Fernandez-Corbaton, I.; Alù, A.; Toscano, A.; Bilotti, F.; Rockstuhl, C., Tunable Scattering Cancellation Cloak with Plasmonic Ellipsoids in the Visible. *Physical Review B* **2016**, *93*, 245127.
65. Park, J.; Lu, W., Orientation of Core-Shell Nanoparticles in an Electric Field. *Applied Physics Letters* **2007**, *91*, 053113.
66. Saeidi, C.; van der Weide, D., Nanoparticle Array Based Optical Frequency Selective Surfaces: Theory and Design. *Opt. Express* **2013**, *21*, 16170-16180.
67. Monti, A.; Alù, A.; Toscano, A.; Bilotti, F., Optical Invisibility through Metasurfaces Made of Plasmonic Nanoparticles. *Journal of Applied Physics* **2015**, *117*, 123103.
68. Monti, A.; Toscano, A.; Bilotti, F., Exploiting the Surface Dispersion of Nanoparticles to Design Optical-Resistive Sheets and Salisbury Absorbers. *Opt. Lett.* **2016**, *41*, 3383-3386.
69. Sherry, L. J.; Chang, S.-H.; Schatz, G. C.; Van Duyne, R. P.; Wiley, B. J.; Xia, Y., Localized Surface Plasmon Resonance Spectroscopy of Single Silver Nanocubes. *Nano Letters* **2005**, *5*, 2034-2038.
70. Jr., G. E. J.; Boatner, L. A.; Budai, J. D.; Jeong, B.-S.; Norton, D. P., Spectroscopic Ellipsometry of Thin Film and Bulk Anatase (TiO₂). *Journal of Applied Physics* **2003**, *93*, 9537-9541.
71. Yousif, H. A.; Köhler, S., Scattering by Two Penetrable Cylinders at Oblique Incidence. I. The Analytical Solution. *J. Opt. Soc. Am. A* **1988**, *5*, 1085-1096.
72. Felbacq, D.; Tayeb, G.; Maystre, D., Scattering by a Random Set of Parallel Cylinders. *J. Opt. Soc. Am. A* **1994**, *11*, 2526-2538.
73. Cooray, M. F. R.; Ciric, I. R., Electromagnetic Wave Scattering by a System of Two Spheroids of Arbitrary Orientation. *IEEE Transactions on Antennas and Propagation* **1989**, *37*, 608-618.
74. Yurkin, M. A.; Hoekstra, A. G., The Discrete Dipole Approximation: An Overview and Recent Developments. *Journal of Quantitative Spectroscopy and Radiative Transfer* **2007**, *106*, 558-589.
75. Sullivan, D. M., *Electromagnetic Simulation Using the Fdtd Method*; John Wiley & Sons, 2013.
76. Teixeira, F. L., Fdtd/Fetd Methods: A Review on Some Recent Advances and Selected Applications. *Journal of Microwaves, Optoelectronics and Electromagnetic Applications (JMoe)* **2007**, *6*, 83-95.
77. Mishchenko, M. I.; Travis, L. D., T-Matrix Computations of Light Scattering by Large Spheroidal Particles. *Optics communications* **1994**, *109*, 16-21.
78. Girard, C.; Dereux, A., Near-Field Optics Theories. *Reports on Progress in Physics* **1996**, *59*, 657-699.
79. Wriedt, T., A Review of Elastic Light Scattering Theories. *Particle & Particle Systems Characterization* **1998**, *15*, 67-74.
80. Taflove, A.; Hagness, S. C., *Computational Electrodynamics: The Finite-Difference Time-*

Domain Method, Artech house, 2005.

81. Kane, Y., Numerical Solution of Initial Boundary Value Problems Involving Maxwell's Equations in Isotropic Media. *IEEE Transactions on Antennas and Propagation* **1966**, *14*, 302–307.
82. Rumpf, R. Maxwell's Equations on a Yee Grid. <http://emlab.utep.edu/ee5390cem/Lecture%2011%20-%20Maxwell%27s%20Equations%20on%20a%20Yee%20Grid.pdf> (accessed 6th May 2019).
83. Total-Field Scattered-Field Sources. https://kb.lumerical.com/ref_sim_obj_sources_tfsf.html (accessed 6th May 2019).
84. Berciaud, S.; Cognet, L.; Tamarat, P.; Lounis, B., Observation of Intrinsic Size Effects in the Optical Response of Individual Gold Nanoparticles. *Nano Letters* **2005**, *5*, 515–518.
85. Blaber, M. G.; Arnold, M. D.; Ford, M. J., Search for the Ideal Plasmonic Nanoshell: The Effects of Surface Scattering and Alternatives to Gold and Silver. *The Journal of Physical Chemistry C* **2009**, *113*, 3041–3045.
86. Kreibig, U., Lattice Defects in Small Metallic Particles and Their Influence on Size Effects. *Zeitschrift für Physik B Condensed Matter* **1978**, *31*, 39–47.
87. Mergel, D.; Buschendorf, D.; Eggert, S.; Grammes, R.; Samset, B., Density and Refractive Index of Tio2 Films Prepared by Reactive Evaporation. *Thin Solid Films* **2000**, *371*, 218–224.
88. Fujiwara, H., *Spectroscopic Ellipsometry: Principles and Applications*; John Wiley & Sons, 2007.
89. Siqueiros, J. M.; Regalado, L. E.; Machorro, R., Determination of (N,K) for Absorbing Thin Films Using Reflectance Measurements. *Appl. Opt.* **1988**, *27*, 4260–4264.
90. Thèye, M.-L., Investigation of the Optical Properties of Au by Means of Thin Semitransparent Films. *Physical Review B* **1970**, *2*, 3060–3078.
91. Bashara, N.; Azzam, R., Ellipsometry and Polarized Light. *NH, Amsterdam* **1977**.
92. Tompkins, H. G.; McGahan, W. A., *Spectroscopic Ellipsometry and Reflectometry: A User's Guide*. 1999. New York: John Wiley and Sons, Inc.
93. Fujiwara, H., Introduction. In *Spectroscopic Ellipsometry for Photovoltaics: Volume 1: Fundamental Principles and Solar Cell Characterization*, Fujiwara, H.; Collins, R. W., Eds. Springer International Publishing: Cham, 2018; pp 1–16.
94. Cappellini, G.; Del Sole, R.; Reining, L.; Bechstedt, F., Model Dielectric Function for Semiconductors. *Physical Review B* **1993**, *47*, 9892–9895.
95. Vial, A.; Laroche, T., Description of Dispersion Properties of Metals by Means of the Critical Points Model and Application to the Study of Resonant Structures Using the Fdtd Method. *Journal of Physics D: Applied Physics* **2007**, *40*, 7152–7158.
96. Liu, Y. C.; Hsieh, J. H.; Tung, S. K., Extraction of Optical Constants of Zinc Oxide Thin Films by Ellipsometry with Various Models. *Thin Solid Films* **2006**, *510*, 32–38.
97. Ye, Y.; Chen, T.; Zhen, J.; Xu, C.; Zhang, J.; Li, H., Resonant Scattering of Green Light Enabled by Ag@Tio2 and Its Application in a Green Light Projection Screen. *Nanoscale* **2018**, *10*, 2438–2446.
98. DeVore, J. R., Refractive Indices of Rutile and Sphalerite. *J. Opt. Soc. Am.* **1951**, *41*, 416–419.
99. Seh, Z. W.; Liu, S.; Low, M.; Zhang, S.-Y.; Liu, Z.; Mlayah, A.; Han, M.-Y., Janus Au-Tio2 Photocatalysts with Strong Localization of Plasmonic near-Fields for Efficient Visible-Light Hydrogen Generation. *Advanced Materials* **2012**, *24*, 2310–2314.
100. Lee, K. H.; Ahmed, I.; Goh, R. S. M.; Khoo, E. H.; Li, E. P.; Hung, T. G. G., Implementation of the Fdtd Method Based on Lorentz-Drude Dispersive Model on Gpu for Plasmonics Applications.

Progress In Electromagnetics Research **2011**, *116*, 441-456.

101. Sehmi, H.; Langbein, W.; Muljarov, E., Optimizing the Drude-Lorentz Model for Material Permittivity: Method, Program, and Examples for Gold, Silver, and Copper. *Physical Review B* **2017**, *95*, 115444.

102. Scaffardi, L. B.; Tocho, J. O., Size Dependence of Refractive Index of Gold Nanoparticles. *Nanotechnology* **2006**, *17*, 1309-1315.

103. Powell, M. J., The Bobyqa Algorithm for Bound Constrained Optimization without Derivatives. *Cambridge NA Report NA2009/06, University of Cambridge, Cambridge* **2009**, 26-46.

104. Oldenburg, S. J.; Jackson, J. B.; Westcott, S. L.; Halas, N., Infrared Extinction Properties of Gold Nanoshells. *Applied Physics Letters* **1999**, *75*, 2897-2899.

105. Hentschel, M.; Saliba, M.; Vogelgesang, R.; Giessen, H.; Alivisatos, A. P.; Liu, N., Transition from Isolated to Collective Modes in Plasmonic Oligomers. *Nano Letters* **2010**, *10*, 2721-2726.

106. Jain, P. K.; Eustis, S.; El-Sayed, M. A., Plasmon Coupling in Nanorod Assemblies: Optical Absorption, Discrete Dipole Approximation Simulation, and Exciton-Coupling Model. *The Journal of Physical Chemistry B* **2006**, *110*, 18243-18253.

107. Nordlander, P.; Oubre, C.; Prodan, E.; Li, K.; Stockman, M. I., Plasmon Hybridization in Nanoparticle Dimers. *Nano Letters* **2004**, *4*, 899-903.

108. Verellen, N.; Sonnefraud, Y.; Sobhani, H.; Hao, F.; Moshchalkov, V. V.; Dorpe, P. V.; Nordlander, P.; Maier, S. A., Fano Resonances in Individual Coherent Plasmonic Nanocavities. *Nano Letters* **2009**, *9*, 1663-1667.

109. Mirin, N. A.; Bao, K.; Nordlander, P., Fano Resonances in Plasmonic Nanoparticle Aggregates. *The Journal of Physical Chemistry A* **2009**, *113*, 4028-4034.

110. Yu, H.-L.; Hsiao, C.-C., Comparison of Different Measurement Methods for Transmittance Haze. *Metrologia* **2009**, *46*, S233-S237.

111. Color. <https://en.wikipedia.org/wiki/Color> (accessed 11th May 2019).

112. Averitt, R. D.; Westcott, S. L.; Halas, N. J., Linear Optical Properties of Gold Nanoshells. *JOSA B* **1999**, *16*, 1824-1832.

113. Prodan, E.; Nordlander, P., Structural Tunability of the Plasmon Resonances in Metallic Nanoshells. *Nano Letters* **2003**, *3*, 543-547.

114. Zhou, H. S.; Honma, I.; Komiyama, H.; Haus, J. W., Controlled Synthesis and Quantum-Size Effect in Gold-Coated Nanoparticles. *Physical Review B* **1994**, *50*, 12052-12056.

115. Wang, Y.; Xie, X.; Wang, X.; Ku, G.; Gill, K. L.; O'Neal, D. P.; Stoica, G.; Wang, L. V., Photoacoustic Tomography of a Nanoshell Contrast Agent in the in Vivo Rat Brain. *Nano Letters* **2004**, *4*, 1689-1692.

116. Loo, C.; Lowery, A.; Halas, N.; West, J.; Drezek, R., Immunotargeted Nanoshells for Integrated Cancer Imaging and Therapy. *Nano Letters* **2005**, *5*, 709-711.

117. West, J. L.; Halas, N. J., Engineered Nanomaterials for Biophotonics Applications: Improving Sensing, Imaging, and Therapeutics. *Annual Review of Biomedical Engineering* **2003**, *5*, 285-292.

118. Chen, A. M.; Scott, M. D., Current and Future Applications of Immunological Attenuation Via Pegylation of Cells and Tissue. *BioDrugs* **2001**, *15*, 833-847.

119. Tang, L.; Liu, L.; Elwing, H. B., Complement Activation and Inflammation Triggered by Model Biomaterial Surfaces. *Journal of Biomedical Materials Research* **1998**, *41*, 333-340.

120. Averitt, R. D.; Sarkar, D.; Halas, N. J., Plasmon Resonance Shifts of Au-Coated Au_{20} Nanoshells: Insight into Multicomponent Nanoparticle Growth. *Physical*

Review Letters **1997**, *78*, 4217-4220.

121. Weissleder, R., A Clearer Vision for in Vivo Imaging. *Nature Biotechnology* **2001**, *19*, 316-317.

122. Gall, D., Electron Mean Free Path in Elemental Metals. *Journal of Applied Physics* **2016**, *119*, 085101.

123. Moroz, A., Electron Mean Free Path in a Spherical Shell Geometry. *The Journal of Physical Chemistry C* **2008**, *112*, 10641-10652.

124. Westcott, S. L.; Jackson, J. B.; Radloff, C.; Halas, N. J., Relative Contributions to the Plasmon Line Shape of Metal Nanoshells. *Physical Review B* **2002**, *66*, 155431.

125. Raschke, G., et al., Gold Nanoshells Improve Single Nanoparticle Molecular Sensors. *Nano Letters* **2004**, *4*, 1853-1857.

126. Averitt, R. D.; Westcott, S. L.; Halas, N. J., Linear Optical Properties of Gold Nanoshells. *J. Opt. Soc. Am. B* **1999**, *16*, 1824-1832.

127. Khlebtsov, B. N.; Khlebtsov, N. G., Ultrasharp Light-Scattering Resonances of Structured Nanospheres: Effects of Size-Dependent Dielectric Functions. *Journal of biomedical optics* **2006**, *11*, 044002.

128. Gordon, J. A.; Ziolkowski, R. W., The Design and Simulated Performance of a Coated Nano-Particle Laser. *Opt. Express* **2007**, *15*, 2622-2653.

129. Ramaccia, D.; Toscano, A.; Bilotti, F., Scattering and Absorption from Super-Spherical Nanoparticles: Analysis and Design for Transparent Displays [Invited]. *J. Opt. Soc. Am. B* **2017**, *34*, D62-D67.

130. Wang, W.; Yu, P.; Zhong, Z.; Tong, X.; Liu, T.; Li, Y.; Ashalley, E.; Chen, H.; Wu, J.; Wang, Z., Size-Dependent Longitudinal Plasmon Resonance Wavelength and Extraordinary Scattering Properties of Au Nanobipyramids. *Nanotechnology* **2018**, *29*, 355402.

131. Yu, P.; Zhang, F.; Li, Z.; Zhong, Z.; Govorov, A.; Fu, L.; Tan, H.; Jagadish, C.; Wang, Z., Giant Optical Pathlength Enhancement in Plasmonic Thin Film Solar Cells Using Core-Shell Nanoparticles. *Journal of Physics D: Applied Physics* **2018**, *51*, 295106.

132. Yu, P.; Yao, Y.; Wu, J.; Niu, X.; Rogach, A. L.; Wang, Z., Effects of Plasmonic Metal Core - Dielectric Shell Nanoparticles on the Broadband Light Absorption Enhancement in Thin Film Solar Cells. *Scientific Reports* **2017**, *7*, 7696.

133. Wu, J., et al., Broadband Efficiency Enhancement in Quantum Dot Solar Cells Coupled with Multispiked Plasmonic Nanostars. *Nano Energy* **2015**, *13*, 827-835.

134. Araki, S.; Ishikawa, Y.; Wang, X.; Uenuma, M.; Cho, D.; Jeon, S.; Uraoka, Y., Fabrication of Nanoshell-Based 3d Periodic Structures by Templating Process Using Solution-Derived ZnO. *Nanoscale Research Letters* **2017**, *12*, 419.

135. Sokolov, K.; Follen, M.; Aaron, J.; Pavlova, I.; Malpica, A.; Lotan, R.; Richards-Kortum, R., Real-Time Vital Optical Imaging of Precancer Using Anti-Epidermal Growth Factor Receptor Antibodies Conjugated to Gold Nanoparticles. *Cancer Research* **2003**, *63*, 1999-2004.

136. Ntziachristos, V.; Bremer, C.; Weissleder, R., Fluorescence Imaging with near-Infrared Light: New Technological Advances That Enable in Vivo Molecular Imaging. *European Radiology* **2003**, *13*, 195-208.

137. Hao, J.; Wang, J.; Liu, X.; Padilla, W. J.; Zhou, L.; Qiu, M., High Performance Optical Absorber Based on a Plasmonic Metamaterial. *Applied Physics Letters* **2010**, *96*, 251104.

138. Song, Z.; Wang, K.; Li, J.; Liu, Q. H., Broadband Tunable Terahertz Absorber Based on Vanadium Dioxide Metamaterials. *Opt. Express* **2018**, *26*, 7148-7154.

139. Song, Z.; He, Q.; Xiao, S.; Zhou, L., Making a Continuous Metal Film Transparent Via Scattering Cancellations. *Applied Physics Letters* **2012**, *101*, 181110.
140. Song, Z.; Zhang, B., Wide-Angle Polarization-Insensitive Transparency of a Continuous Opaque Metal Film for near-Infrared Light. *Opt. Express* **2014**, *22*, 6519-6525.
141. Song, Z.; Gao, Z.; Zhang, Y.; Zhang, B., Terahertz Transparency of Optically Opaque Metallic Films. *EPL (Europhysics Letters)* **2014**, *106*, 27005.
142. Song, Z.; Xu, H., Near-Infrared Transparent Conducting Metal Based on Impedance Matching Plasmonic Nanostructures. *EPL (Europhysics Letters)* **2014**, *107*, 57007.
143. Barchiesi, D.; Grosjes, T., *Fitting the Optical Constants of Gold, Silver, Chromium, Titanium, and Aluminum in the Visible Bandwidth*; SPIE, 2014; Vol. 8, p 1-17, 17.
144. Kreibig, U.; Genzel, L., Optical Absorption of Small Metallic Particles. *Surface Science* **1985**, *156*, 678-700.
145. Hövel, H.; Fritz, S.; Hilger, A.; Kreibig, U.; Vollmer, M., Width of Cluster Plasmon Resonances: Bulk Dielectric Functions and Chemical Interface Damping. *Physical Review B* **1993**, *48*, 18178-18188.
146. Philipse, A. P.; Vrij, A., Preparation and Properties of Nonaqueous Model Dispersions of Chemically Modified, Charged Silica Spheres. *Journal of Colloid and Interface Science* **1989**, *128*, 121-136.
147. Philipse, A. P.; Vrij, A., Polydispersity Probed by Light Scattering of Secondary Particles in Controlled Growth Experiments of Silica Spheres. *The Journal of Chemical Physics* **1987**, *87*, 5634-5643.
148. Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L., Optical Absorption Spectra of Nanocrystal Gold Molecules. *The Journal of Physical Chemistry B* **1997**, *101*, 3706-3712.
149. Noguez, C., Surface Plasmons on Metal Nanoparticles: The Influence of Shape and Physical Environment. *The Journal of Physical Chemistry C* **2007**, *111*, 3806-3819.
150. Avrutsky, I., Surface Plasmons at Nanoscale Relief Gratings between a Metal and a Dielectric Medium with Optical Gain. *Physical Review B* **2004**, *70*, 155416.
151. Noginov, M. A.; Zhu, G.; Bahoura, M.; Adegoke, J.; Small, C. E.; Ritzo, B. A.; Drachev, V. P.; Shalaev, V. M., Enhancement of Surface Plasmons in an Ag Aggregate by Optical Gain in a Dielectric Medium. *Opt. Lett.* **2006**, *31*, 3022-3024.
152. Digonnet, M. J., *Rare-Earth-Doped Fiber Lasers and Amplifiers, Revised and Expanded*; CRC press, 2001.
153. Lawandy, N. M., Localized Surface Plasmon Singularities in Amplifying Media. *Applied Physics Letters* **2004**, *85*, 5040-5042.
154. Hide, F.; Schwartz, B. J.; Díaz-García, M. A.; Heeger, A. J., Conjugated Polymers as Solid-State Laser Materials. *Synthetic Metals* **1997**, *91*, 35-40.
155. Li, X. F.; Yu, S. F., Design of Low-Threshold Compact Au-Nanoparticle Lasers. *Opt. Lett.* **2010**, *35*, 2535-2537.
156. Campbell, S. D.; Ziolkowski, R. W., Impact of Strong Localization of the Incident Power Density on the Nano-Amplifier Characteristics of Active Coated Nano-Particles. *Optics Communications* **2012**, *285*, 3341-3352.
157. Zhang, H.; Zhou, J.; Zou, W.; He, M., Surface Plasmon Amplification Characteristics of an Active Three-Layer Nanoshell-Based Spaser. *Journal of Applied Physics* **2012**, *112*, 074309.

158. Wu, D. J.; Cheng, Y.; Wu, X. W.; Liu, X. J., An Active Metallic Nanomatryushka with Two Similar Super-Resonances. *Journal of Applied Physics* **2014**, *116*, 013502.
159. Noginov, M. A.; Zhu, G.; Belgrave, A. M.; Bakker, R.; Shalae, V. M.; Narimanov, E. E.; Stout, S.; Herz, E.; Suteewong, T.; Wiesner, U., Demonstration of a Spaser-Based Nanolaser. *Nature* **2009**, *460*, 1110.
160. Bergman, D. J.; Stockman, M. I., Surface Plasmon Amplification by Stimulated Emission of Radiation: Quantum Generation of Coherent Surface Plasmons in Nanosystems. *Physical Review Letters* **2003**, *90*, 027402.
161. Liu, S.-Y.; Li, J.; Zhou, F.; Gan, L.; Li, Z.-Y., Efficient Surface Plasmon Amplification from Gain-Assisted Gold Nanorods. *Opt. Lett.* **2011**, *36*, 1296-1298.
162. Stockman, M. I., The Spaser as a Nanoscale Quantum Generator and Ultrafast Amplifier. *Journal of Optics* **2010**, *12*, 024004.
163. Li, Z.-Y.; Xia, Y., Metal Nanoparticles with Gain toward Single-Molecule Detection by Surface-Enhanced Raman Scattering. *Nano Letters* **2010**, *10*, 243-249.
164. Klyshko, D. N., *Photons Nonlinear Optics*; Routledge, 2018.
165. Schanda, J., Cie Color-Rendering Index. *Encyclopedia of Color Science and Technology* **2014**, 1-5.
166. Zhang, M.; Lin, G.; Dong, C.; Wen, L., Amorphous Tio₂ Films with High Refractive Index Deposited by Pulsed Bias Arc Ion Plating. *Surface and Coatings Technology* **2007**, *201*, 7252-7258.
167. Taflove, A.; C. Hagness, S., *Computational Electrodynamics: The Finite-Difference Time-Domain Method. 2nd Ed*, 2000; Vol. 67-106.
168. Kreibig, U., Electronic Properties of Small Silver Particles: The Optical Constants and Their Temperature Dependence. *Journal of Physics F: Metal Physics* **1974**, *4*, 999-1014.
169. Zhang, S.; Bao, K.; Halas, N. J.; Xu, H.; Nordlander, P., Substrate-Induced Fano Resonances of a Plasmonic Nanocube: A Route to Increased-Sensitivity Localized Surface Plasmon Resonance Sensors Revealed. *Nano Letters* **2011**, *11*, 1657-1663.
170. Bottomley, A.; Ianoul, A., Reflection and Absorption Spectra of Silver Nanocubes on a Dielectric Substrate: Anisotropy, Angle, and Polarization Dependencies. *The Journal of Physical Chemistry C* **2014**, *118*, 27509-27515.
171. Knight, M. W.; Wu, Y.; Lassiter, J. B.; Nordlander, P.; Halas, N. J., Substrates Matter: Influence of an Adjacent Dielectric on an Individual Plasmonic Nanoparticle. *Nano Letters* **2009**, *9*, 2188-2192.
172. Wu, Y.; Nordlander, P., Finite-Difference Time-Domain Modeling of the Optical Properties of Nanoparticles near Dielectric Substrates. *The Journal of Physical Chemistry C* **2010**, *114*, 7302-7307.
173. Vernon, K. C.; Funston, A. M.; Novo, C.; Gómez, D. E.; Mulvaney, P.; Davis, T. J., Influence of Particle-Substrate Interaction on Localized Plasmon Resonances. *Nano Letters* **2010**, *10*, 2080-2086.
174. Ye, Y.; Chen, T. P., Selective Scattering of Blue and Red Light Based on Silver and Gold Nanocubes. *ECS Journal of Solid State Science and Technology* **2019**, *8*, R51-R57.
175. Okimura, K., Low Temperature Growth of Rutile Tio₂ Films in Modified Rf Magnetron Sputtering. *Surface and Coatings Technology* **2001**, *135*, 286-290.

Appendix A

80 nm Silica Core with 15 nm Gold Nanoshell, PVP

Lot Number: JAG0399

Total Diameter (TEM):	113 ± 5 nm	Mass Concentration (Au):	0.020 mg/mL
Coefficient of Variation:	4.6 %	Hydrodynamic Diameter:	144 nm
Core Diameter (TEM):	80 ± 6 nm	Zeta Potential:	-35 mV
Shell Thickness (Calc'd):	16 nm	pH of Solution:	5.6
Surface Area (Calc'd):	4.0 m ² /g	Particle Surface:	PVP
Particle Concentration:	2.1E+09 particles/mL	Solvent:	Milli-Q Water

Size Distribution

Optical Properties

Characterization Instrumentation

Diameter and Size Statistics:	JEOL 1010 Transmission Electron Microscope
Mass Concentration:	Thermo Fisher X Series 2 ICP-MS
Spectral Properties:	Agilent 8453 UV-Visible Spectrometer
Hydrodynamic Diameter/Zeta Potential:	Malvern Zetasizer Nano ZS.

Shake vigorously before use. Bath sonicate if needed. Storage: 2-8 °C. DO NOT FREEZE.

Produced under license to United States patent numbers 6,344,272, 6,685,986, and 7,371,457.

These nanoComposix products are to be used for research purposes only and are not to be used for any commercial purposes.

Gold Nanoshells, Peak Absorbance @ 660 nm, PVP, NanoXact™

Lot Number: JRC0466

Total Diameter (TEM):	137 ± 5 nm	Mass Concentration (Au):	0.050 mg/mL
Coefficient of Variation:	3.9 %	Hydrodynamic Diameter:	157 nm
Core Diameter (TEM):	79 ± 3 nm	Zeta Potential:	-31 mV
Shell Thickness (Calc'd):	29 nm	pH of Solution:	5.9
Surface Area (Calc'd):	2.7 m ² /g	Particle Surface:	PVP 40 kDa (Polymer)
Particle Concentration (Calc'd):	2.4E+09 particles/mL	Solvent:	Milli-Q Water

Size Distribution

Optical Properties

Characterization Instrumentation

Diameter and Size Statistics:	JEOL 1010 Transmission Electron Microscope
Mass Concentration:	Thermo Fisher X Series 2 ICP-MS
Spectral Properties:	Agilent 8453 UV-Visible Spectrometer
Hydrodynamic Diameter/Zeta Potential:	Malvern Zetasizer Nano ZS
pH:	Horiba - Laqua Twin pH Meter

Shake vigorously before use. Bath sonicate if needed. Storage: 2-8 °C. DO NOT FREEZE.

Produced under license to United States patent numbers 6,344,272, 6,685,986, and 7,371,457.

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Gold Nanoshells, Peak Absorbance @ 660 nm, PEG, NanoXact™

Lot Number: JRC0398

Total Diameter (TEM):	159 ± 11 nm	Mass Concentration (Au):	0.051 mg/mL
Coefficient of Variation:	6.7 %	Hydrodynamic Diameter:	181 nm
Core Diameter (TEM):	88 ± 3 nm	Zeta Potential:	-28 mV
Shell Thickness (Calc'd):	36 nm	pH of Solution:	5.5
Surface Area (Calc'd):	2.3 m ² /g	Particle Surface:	mPEG 5 kDa (Polymer)
Particle Concentration (Calc'd):	1.5E+09 particles/mL	Solvent:	Milli-Q Water

Size Distribution **Optical Properties** **Characterization Instrumentation**

Diameter and Size Statistics:	JEOL 1010 Transmission Electron Microscope
Mass Concentration:	Thermo Fisher X Series 2 ICP-MS
Spectral Properties:	Agilent 8453 UV-Visible Spectrometer
Hydrodynamic Diameter/Zeta Potential:	Malvern Zetasizer Nano ZS
pH:	Horiba - Laqua Twin pH Meter

Shake vigorously before use. Bath sonicate if needed. Storage: 2-8 °C. DO NOT FREEZE.

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