**SECOND HARMONIC GENERATION OF
CHIRAL-MODIFIED SILVER NANOPARTICLES**

by

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Abstract

Chiral molecules, which exist under enantiomers with non-mirror-symmetrical structures, have been the subject of intense research for their linear and nonlinear optical activities. Cysteine is such a chiral amino acid found as a building block of proteins throughout human bodies. Second harmonic generation (SHG) has been considered to investigate chiral molecules. SHG from metallic nanoparticles is promising for nanoplasmonics and photonic nanodevice applications. Therefore, it's desirable to combine and study nonlinear properties due to both chirality and metallic nanoparticles, and help developing an alternatively optical diagnostic of chiral molecules.

Our experiments are carried out with the FemtoFiber Scientific FFS laser system. SHG of silver nanoparticles (Ag NPs) modified by either L-Cysteine (L-C) or D-Cysteine (D-C) is observed, where L-Cysteine and D-Cysteine are a pair of enantiomers. Ag NPs are deposited through Vacuum Thermal Evaporation, controlled under different deposition thicknesses. UV-Vis/IR spectra and AFM are used to characterize Ag NPs under different conditions. Transmitted SHG measurements dependent on incidence are recorded with standard lock-in techniques.

Deposition thickness of vacuum thermal evaporation plays an important role in forming diverse Ag NPs, which strongly imparts the intensity of SHG. Second harmonic intensity as a function of the incident angle presents similar results for Ag NPs with or without L-Cysteine or D-Cysteine modification, in the output of p- and s-polarization. However, we monitor reversed rotation difference in second harmonic intensities at linearly $+45^\circ$ and -45°

polarization for L-C/Ag NPs and D-C/Ag NPs, while there's no difference at linearly $+45^\circ$ and -45° polarization for Ag NPs alone. This optical rotation difference in SHG is termed as SHG-ORD. Also, for second harmonic light fixed at p-polarization, L-C/Ag NPs and D-C/Ag NPs exhibit a reversely net difference for SHG excited by right and left circular polarization, which is termed as SHG-CD. Experiments on SHG-ORD of chiral-modified Ag NPs by a mixture of L-Cysteine and D-Cysteine further help verifying the existence of chirality in chiral-modified Ag NPs.

As a conclusion, SHG efficiently probed and distinguished L-Cysteine from D-Cysteine in chiral-modified Ag NPs.

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Statement of Originality

I hereby certify that all of the work described within this thesis is the original work of the author under the supervision of Dr. Jean-Michel Nunzi. Any published (or unpublished) ideas and/or techniques from the work of others are fully acknowledged in accordance with the standard referencing practices.

(Yue Tao)

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List of Abbreviations

Abs	Absorbance
AFM	Atomic Force Microscopy
Ag NPs	Silver Nanoparticles
D-C	D-Cysteine
D-C/Ag NPs	Ag NPs modified by D-Cysteine
DFG	Difference-frequency Generation
IR	Infrared
L-C	L-Cysteine
L-C/Ag NPs	Ag NPs modified by L-Cysteine
LSPR	Localized Surface Plasmon Resonance
MAX	Maximum
NLO	Nonlinear Optical
OFC	Optical Frequency Conversion
OPA	Optical Parametric Amplifier
OPO	Optical Parametric Oscillator
OR	Optical Rectification
PMT	Photomultiplier Tube
S	Sulfur
SERS	Surface-enhanced Raman Scattering
SFG	Sum-frequency Generation
SH Intensity	Second harmonic Intensity
SHG	Second Harmonic Generation
SHG-ORD	Second Harmonic Generation- Optical Rotatory Difference
SHG-CD	Second Harmonic Generation- Circular Difference
SIF	Silver Island Film
SPs	Surface Plasmons

SPR	Surface Plasmon Resonance
TE	Transverse Electric
THG	Third Harmonic Generation
TM	Transverse Magnetic
UV-Vis	Ultraviolet-Visible

Chapter 1

Introduction and Literature Review

1.1 Overview of Nonlinear Optics

1.1.1 History

Nonlinear optics attracted numerous studies since the invention of laser in 1958. Before that, linear optics dominates the rule of light-matter interaction, where the optical frequency of light doesn't change during propagation like reflection, absorption, and transmission etc., and optical properties of matter have no dependency with the intensity of incident light.¹ However, in 1961, by using a high-power Ruby laser, P. A. Franken *et al.* first demonstrated the nonlinear optical (NLO) phenomenon in the form of second harmonic generation (SHG) observed in the bulk region of a quartz crystal, where the frequency of the incident light was doubled due to the coherent mixing of two optical electric fields. Their work also summarized that the production of SHG requires optically absorbing material with a nonlinear dielectric coefficient and transparency to both the fundamental and harmonic frequencies.² Therefore, NLO effects arise when a sufficiently intense electromagnetic field, which typically means laser, interacts with optical materials and produces nonlinear perturbations in the optical properties of materials.³

After this discovery, N. Bloembergen *et al.* theoretically formulated the physical principles of nonlinear optics, which connects the traditional linear optics and the new world of nonlinear phenomena.⁴ Within the next several decades, many other types of

lasers were developed⁵ and used for the observation of third harmonic generation (THG),⁶ sum frequency generation (SFG),⁷ difference frequency generation (DFG),⁸ optical rectification (OR)⁹ and multi-photon absorption processes¹⁰ etc. At the same time, varieties of NLO materials have been investigated both experimentally and theoretically, including inorganic or organic crystals, semiconductor or metal nanostructures, polymer thin films and chiral surfaces etc.^{11,12,13,14} Nonlinear optical techniques also become promising in many applications, such as photonic devices, nonlinear spectroscopy, electro-optic detection, optical switching and so on.^{15,16,17}

Nowadays, nonlinear optics has become an important branch of physics.¹⁸ As what Y.R. Shen pointed out, “Physics would be dull and life most unfulfilling if all physical phenomena around us were linear. Fortunately, we are living in a nonlinear world.”¹⁹

1.1.2 Basic theory: wave equation and nonlinear polarization

All theory illustrations in section 1.1 are mainly referred to Nonlinear Optics written by R. W. Boyd.²⁰

Optical phenomena in the form of electromagnetic radiation can be represented with Maxwell’s equations:

$$\begin{aligned}\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t}, \\ \nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}, \\ \nabla \cdot \mathbf{D} &= \rho, \\ \nabla \cdot \mathbf{B} &= 0.\end{aligned}\tag{1.1}$$

where $\mathbf{E}$ is the electric field, $\mathbf{H}$ is the magnetic field and ρ is the free charge density. The electric displacement $\mathbf{D}$, magnetic induction $\mathbf{B}$ and free electric current density $\mathbf{J}$ are described in the matter equations as following:

$$\begin{aligned}\mathbf{D} &= \varepsilon_0 \mathbf{E} + \mathbf{P}, \\ \mathbf{B} &= \mu_0 \mathbf{H} + \mu_0 \mathbf{M}, \\ \mathbf{J} &= \sigma \mathbf{E}.\end{aligned}\tag{1.2}$$

where ε_0 is the vacuum permittivity, μ_0 is the vacuum permeability, σ is the medium conductivity, $\mathbf{M}$ is the magnetization and $\mathbf{P}$ is the induced polarization. All equations and calculations throughout this thesis are described in SI units.

The polarization $\mathbf{P}$, defined as the dipole moment per unit volume, is generated from electric field $\mathbf{E}$ induced dipoles. In linear optics, $\mathbf{P}$ is considered to be linearly related to $\mathbf{E}$.

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E}\tag{1.3}$$

where χ is called the susceptibility of a linear or isotropic material. It is a good approximation for light-matter interaction occurred under a low electric field. However, for an anisotropic material, $\mathbf{P}$ is considered to include nonlinear terms and expanded in a Taylor series.

$$\begin{aligned}\mathbf{P} &= \mathbf{P}_L + \mathbf{P}_{NL} \\ &= \varepsilon_0 \left[\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \dots \right]\end{aligned}\tag{1.4}$$

where $\mathbf{P}_L$ represents the linear and $\mathbf{P}_{NL}$ is the sum of all nonlinear terms. The material is regarded as lossless. $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are known as the linear susceptibility, second-

and third-order nonlinear optical susceptibilities, which represent the material's response to the incident electromagnetic field. If the electric field is very intense, $\mathbf{P}_{NL}$ cannot be ignored.

To look into the light propagation through a nonlinear medium, let us consider a non-magnetic and source-free medium, where there are no free charges and currents. Equation (1.1) becomes

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (1.5)$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}, \quad (1.6)$$

$$\nabla \cdot \mathbf{D} = 0, \quad (1.7)$$

$$\nabla \cdot \mathbf{B} = 0. \quad (1.8)$$

By taking the curl of equation (1.5) and using equation (1.6), the expression below is obtained.

$$\bar{\nabla} \times \bar{\nabla} \times \mathbf{E} = -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2} \quad (1.9)$$

R. W. Boyd²⁰ further illustrated equation (1.9) in the following form, by incorporating equations (1.2), (1.4) and (1.7).

$$\nabla^2 \mathbf{E} - \frac{\epsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \mathbf{P}_{NL}}{\partial t^2} \quad (1.10)$$

where ε is the relative permittivity depending on different materials. Wave equation (1.10) indicates that the nonlinear polarization $\mathbf{P}_{NL}$ behaves as the source term in an inhomogeneous wave equation.

1.1.3 Properties of nonlinear optical susceptibilities

If the material is not lossless, nonlinear optical susceptibilities mentioned in equation (1.4) turn out to be complex in a relation with complex amplitudes of $\mathbf{E}$ and $\mathbf{P}$. As the electric field $\mathbf{E}$ can be described by the discrete sum of the positive and negative frequency components, R. W. Boyd²⁰ express the nonlinear polarization $\mathbf{P}_{NL}$ using the same convention as below.

$$\mathbf{P}_{NL} = \sum_n \mathbf{P}(\omega_n) e^{-i\omega_n t} = \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots + \mathbf{P}^{(n)} \quad (1.11)$$

where $\mathbf{P}^{(n)}$ is the nth-order polarization. Taking the second-order polarization $\mathbf{P}^{(2)}$ as an example, we will only introduce and discuss the second-order susceptibility in this section.

Indices i, j, k are dummy and used to refer to Cartesian components of the polarization or electric field, where the summation of all components over the Cartesian coordinates including frequency differences can represent $\mathbf{P}^{(2)}$ in scalar quantities. For example, the scalar component $P_i^{(2)}$ can be expressed as

$$P_i^{(2)}(\omega_n + \omega_m) = D\varepsilon_0 \sum_{jk} \sum_{nm} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m) \quad (1.12)$$

where $\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)$ is the second-order susceptibility tensor, and ω_n, ω_m are frequencies of different electric fields, which can be either positive or negative. Cartesian indices i, j, k are respectively related to $\omega_n + \omega_m, \omega_n$ and ω_m . D is the degeneracy factor, whose value depends on the difference of frequencies. In the second-order NLO, D is defined as the following.

$$D = \begin{cases} 1 & m = n \\ 2 & m \neq n \end{cases} \quad (1.13)$$

Because indices i, j, k can independently be X Y Z and frequencies can be either positive or negative in the rule of math, physical limit and symmetry properties are applied to restrict the number of tensors.

First, the electric field is real and the polarization has also to be measurable, where the negative frequency doesn't exist in reality. Based on this evolution of equation (1.12), positive and negative frequencies incorporated in the susceptibility are related accordingly.

$$\chi_{ijk}^{(2)}(-\omega_n - \omega_m, -\omega_n, -\omega_m) = \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)^* \quad (1.14)$$

Second, physically, the induced order of electric fields with different frequencies should not influence the production of polarization. Therefore, the intrinsic permutation symmetry is considered and results in the free interchange between ω_n and ω_m components in the susceptibility.

$$\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) = \chi_{ikj}^{(2)}(\omega_n + \omega_m, \omega_m, \omega_n) \quad (1.15)$$

Third, for lossless materials where all components of the susceptibility are real, full permutation symmetry is applied. As shown in equation (1.15), all frequency components can be interchanged freely by adding reversed signs.

$$\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) = \chi_{jki}^{(2)}(-\omega_n, \omega_m, -\omega_n - \omega_m) = \chi_{kij}^{(2)}(\omega_m, \omega_n + \omega_m, -\omega_n) \quad (1.16)$$

The last symmetry condition is called the Kleinman's symmetry, which requires that the optical frequency is much lower than the lowest resonant frequency of the material. So the susceptibility always stays the same for any frequency and any indices i j k.

$$\chi_{ijk}^{(2)} = \chi_{jki}^{(2)} = \chi_{kij}^{(2)} = \chi_{ikj}^{(2)} = \chi_{kji}^{(2)} = \chi_{jik}^{(2)} \quad (1.17)$$

Accordingly, the second-order polarization becomes

$$\mathbf{P}^{(2)} = \varepsilon_0 \chi^{(2)} \mathbf{E}^2(t) \quad (1.18)$$

where $\chi^{(2)}$ is a constant.

When the Kleinman's symmetry is true, the scalar component of nonlinear polarization becomes²⁰:

$$P_i(\omega_n + \omega_m) = \varepsilon_0 \sum_{jk} \sum_{nm} \chi_{ijk} E_j(\omega_n) E_k(\omega_m) \quad (1.19)$$

1.1.4 Second-order nonlinear optical processes

In this section, fundamental second-order NLO processes are briefly described and SHG will be further discussed in the next section.

Figure 1.1 Geometry (left) and energy-level diagram (right) of SFG

In SFG, Figure 1.1 shows that two pump optical fields with different frequencies can interact in a second-order nonlinear medium and produce a new optical field with a summation frequency of two fundamental frequencies. Polarization of SFG can be expressed as

$$\mathbf{P}(\omega_3 = \omega_1 + \omega_2) = 2\varepsilon_0\chi^{(2)}\mathbf{E}(\omega_1)\mathbf{E}(\omega_2) \quad (1.20)$$

The reverse of this process, called optical frequency conversion (OFC), is widely used in generating laser sources with tunable wavelengths, such as a wavelength in the ultraviolet region.

Two pump optical fields can also produce a new optical field whose frequency is the difference between fundamental frequencies, as illustrated in Figure 1.2.

Figure 1.2 Geometry (left) and energy-level diagram (right) of DFG

Polarization of DFG can be expressed as

$$\mathbf{P}(\omega_3 = \omega_1 - \omega_2) = 2\varepsilon_0\chi^{(2)}\mathbf{E}(\omega_1)\mathbf{E}^*(\omega_2) \quad (1.21)$$

From the energy-level diagram of DFG, it can be seen that fundamental photons with a lower frequency are created while fundamental photons with a high frequency are destroyed. This is called the optical parametric amplification, where photons with a lower frequency are amplified and two-photon emission occurs. Thus, DFG can be applied to optical parametric amplifier (OPA), optical parametric oscillator (OPO) etc.

Comparably, if the pump optical field only has one frequency as shown in Figure 1.3, in the second-order nonlinear medium, each pump can generate a second harmonic optical field with a double frequency than the original. The nature of SHG is reflected from the energy-level diagram, where two fundamental photons destruct and a double-frequency photon is created almost simultaneously during the energy transition. Therefore, SHG is a coherent process.

Figure 1.3 Geometry (left) and energy-level diagram (right) of SHG
Polarization of SHG can be expressed as

$$\mathbf{P}(\omega_2 = 2\omega_1) = \varepsilon_0\chi^{(2)}\mathbf{E}^2(\omega_1) \quad (1.22)$$

The last second-order NLO process introduced here is OR as described in Figure 1.4. When an intense optical field goes through a nonlinear material, a direct current voltage can be detected across the surfaces, which looks like examining a capacitor with nonlinear media inside.

Figure 1.4 Schematic generation of OR

Mathematical description of OR can be expressed as

$$\mathbf{P}(0) = \varepsilon_0 \chi^{(2)} \mathbf{E}(\omega) \mathbf{E}^*(\omega) = \varepsilon_0 \chi^{(2)} \mathbf{E}^2(\omega) \quad (1.23)$$

where $\mathbf{P}(0)$ corresponds to a steady polarization density in the presence of a strong electric field $\mathbf{E}(0)$ and a zero radiation field.

1.2 Second Harmonic Generation

1.2.1 General description of second harmonic generation in noncentrosymmetric media

SHG theory has been fully described by R. W. Boyd²⁰ based on the calculation of wave equations in section 1.1.2. Here we will only simply describe SHG by inducing spatial symmetries of materials.

SHG written in the way of matrix is

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = \varepsilon_0 \begin{bmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & \chi_{xyz} & \chi_{xxz} & \chi_{xxy} \\ \chi_{yxx} & \chi_{yyy} & \chi_{yzz} & \chi_{yzy} & \chi_{yxz} & \chi_{yyx} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & \chi_{zyz} & \chi_{zxz} & \chi_{zxy} \end{bmatrix} \begin{bmatrix} E_x(\omega)^2 \\ E_y(\omega)^2 \\ E_z(\omega)^2 \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{bmatrix} \quad (1.24)$$

where independent non-vanishing elements differ with structure symmetries of materials.

By judging the existence of an inversion center, nonlinear materials can be classified as centrosymmetric and noncentrosymmetric. For example, an interface which is between air and water is noncentrosymmetric, while air and water are centrosymmetric. Based on the model of a classical anharmonic oscillator, R. W. Boyd²⁰ has proved that for a noncentrosymmetric medium, second-order NLO is the lowest order which contributes to a nonlinear polarization. However, for centrosymmetric media, third-order NLO contributes to the lowest order of a nonlinear polarization.

The conclusion can also be given based on equation (1.24). For a centrosymmetric material, if the sign of optical field is changed from $\mathbf{E}$ to $-\mathbf{E}$, the sign of polarization must also change reversely due to the inversion symmetry. Hence, we have

$$-\mathbf{P}(\omega_2 = 2\omega_1) = \varepsilon_0 \chi^{(2)} [-\mathbf{E}(\omega_1)]^2 = \varepsilon_0 \chi^{(2)} [\mathbf{E}(\omega_1)]^2 \quad (1.25)$$

where $\mathbf{P}$ must equal $-\mathbf{P}$, if $\mathbf{P}$ can vanish identically. According to this classic illustration, it concludes that $\chi^{(2)}$ of SHG in a centrosymmetric material is always zero.²¹

Respectively, noncentrosymmetric materials possess a nonzero $\chi^{(2)}$, which corresponds to SHG. According to the point group theory, materials are classified with different symmetry elements. Noncentrosymmetric structures include for instance, a proper axis symmetry represented by C_n (n is an integer). Compounds in this group only have the C_n axis, where chiral molecules are typical examples with C_n and would be further introduced in section 1.5. Comparably, another example of noncentrosymmetric structures in the C class is $C_{n\infty}$, which not only has the C_n axis but also n planes of symmetry containing the C_n axis. In $C_{n\infty}$, no symmetry plane is perpendicular to the C_n axis. Here we will give simplified sample descriptions of SHG from nonlinear materials with $C_{\infty v}$ and C_∞ symmetries. $C_{\infty v}$ symmetry means that the broken symmetry is along the surface normal and isotropy exists in plane, which are normally used to describe achiral molecules. Respectively, C_∞ is used to represent chiral molecules deprived of mirror symmetry.²²

For $C_{\infty v}$ symmetry, when the Kleinman symmetry holds, the second-order susceptibility tensor $\chi^{(2)}$ is given by

$$\chi^{(2)} = \begin{bmatrix} 0 & 0 & 0 & 0 & \chi_{xzx} & 0 \\ 0 & 0 & 0 & \chi_{yzy} & 0 & 0 \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & 0 & 0 \end{bmatrix} \quad (1.26)$$

where non-vanishing elements are $\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)}$, $\chi_{yzy}^{(2)} = \chi_{yyz}^{(2)} = \chi_{xxz}^{(2)} = \chi_{xzx}^{(2)}$ and $\chi_{zzz}^{(2)}$. In this case, equation (1.26) would be

$$\begin{bmatrix} P_X(2\omega) \\ P_Y(2\omega) \\ P_Z(2\omega) \end{bmatrix} = \varepsilon_0 \begin{bmatrix} 0 & 0 & 0 & 0 & \chi_{XZX} & 0 \\ 0 & 0 & 0 & \chi_{YZY} & 0 & 0 \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_X(\omega)^2 \\ E_Y(\omega)^2 \\ E_Z(\omega)^2 \\ 2E_Y(\omega)E_Z(\omega) \\ 2E_X(\omega)E_Z(\omega) \\ 2E_X(\omega)E_Y(\omega) \end{bmatrix} \quad (1.27)$$

which gives

$$P_X(2\omega) = 2\varepsilon_0 \chi_{XZX}^{(2)} E_X(\omega) E_Z(\omega) \quad (1.28)$$

$$P_Y(2\omega) = 2\varepsilon_0 \chi_{YZY}^{(2)} E_Y(\omega) E_Z(\omega) \quad (1.29)$$

$$P_Z(2\omega) = \varepsilon_0 [\chi_{ZXX}^{(2)} E_X(\omega)^2 + \chi_{ZYY}^{(2)} E_Y(\omega)^2 + \chi_{ZZZ}^{(2)} E_Z(\omega)^2] \quad (1.30)$$

Comparably, for C_∞ symmetry, additional non-vanishing elements of $\chi^{(2)}$ have to be considered.

$$\chi_{XYZ}^{(2)} = -\chi_{YXZ}^{(2)} = -\chi_{YZX}^{(2)} = \chi_{XZY}^{(2)} \quad (1.31)$$

So the second-order susceptibility tensor $\chi^{(2)}$ becomes

$$\chi^{(2)} = \begin{bmatrix} 0 & 0 & 0 & \chi_{XYZ} & \chi_{XZX} & 0 \\ 0 & 0 & 0 & \chi_{YZY} & \chi_{YZX} & 0 \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & 0 & 0 & \chi_{ZXY} \end{bmatrix} \quad (1.32)$$

Similarly, equation (1.24) in this case would be

$$\begin{bmatrix} P_X(2\omega) \\ P_Y(2\omega) \\ P_Z(2\omega) \end{bmatrix} = \varepsilon_0 \begin{bmatrix} 0 & 0 & 0 & \chi_{XYZ} & \chi_{XZX} & 0 \\ 0 & 0 & 0 & \chi_{YZY} & \chi_{YZX} & 0 \\ \chi_{ZXX} & \chi_{ZYY} & \chi_{ZZZ} & 0 & 0 & \chi_{ZXY} \end{bmatrix} \begin{bmatrix} E_X(\omega)^2 \\ E_Y(\omega)^2 \\ E_Z(\omega)^2 \\ 2E_Y(\omega)E_Z(\omega) \\ 2E_X(\omega)E_Z(\omega) \\ 2E_X(\omega)E_Y(\omega) \end{bmatrix} \quad (1.33)$$

which gives

$$P_X(2\omega) = 2\varepsilon_0[\chi_{XYZ}^{(2)}E_Y(\omega)E_Z(\omega) + \chi_{XZX}^{(2)}E_X(\omega)E_Z(\omega)] \quad (1.34)$$

$$P_Y(2\omega) = 2\varepsilon_0[\chi_{YZY}^{(2)}E_Y(\omega)E_Z(\omega) + \chi_{YZX}^{(2)}E_X(\omega)E_Z(\omega)] \quad (1.35)$$

$$P_Z(2\omega) = \varepsilon_0[\chi_{ZXX}^{(2)}E_X(\omega)^2 + \chi_{ZYY}^{(2)}E_Y(\omega)^2 + \chi_{ZZZ}^{(2)}E_Z(\omega)^2 + 2\chi_{ZXY}^{(2)}E_X(\omega)E_Y(\omega)] \quad (1.36)$$

By comparing each scalar component of polarization, it can be seen that C_∞ symmetry possesses additional contributions to the nonlinear polarization than $C_{\infty v}$. Further calculation of $\chi^{(2)}$ and second harmonic intensity will be discussed with experimental results accordingly in Chapter 4.

1.2.2 Applications

Noncentrosymmetric SHG materials could vary from inorganic crystals, metallic thin films to other organic nonlinear materials, which have been studied both experimentally and theoretically. SHG is mainly applied to build wavelength conversion laser system, probe surface or interface properties and developed into nonlinear imaging microscopy.

Second harmonic laser

Second harmonic lasers are usually achieved by placing NLO crystals inside the resonator system, where efficient phase matching condition is strictly required by tuning the temperature or angle of crystals. The traditional phase matching condition in SHG is defined as

$$\delta\mathbf{k} = \mathbf{k}_2 - 2\mathbf{k}_1 = 0 \quad (1.37)$$

where $\mathbf{k}_1$ and $\mathbf{k}_2$ are wavevectors of the fundamental and second-harmonic beams respectively.²³ Different NLO crystals work at specific frequency converted wavelengths. As shown in Table 1.1, some typically useful NLO crystals are selected by working wavelengths.

<i>NLO crystals</i>	<i>Approximate second harmonic wavelength range (nm)</i>
BBO	200-350
LBO	300-625
KTP, PPKTP	400-625
KNbO ₃	425-625
PPLN	475-625

Table 1.1 TOPTICA's selection of NLO crystals depending on the wavelength.²⁴

Surface/Interface probe

Due to the advantages of high sensitivity and non-destructivity, SHG technology is a useful method to probe properties of surfaces or interfaces in surface chemistry.²⁵ As it is known, the second order susceptibility is directly related to the surface/interface structures. If a new layer of molecules with $\chi_{\Lambda}^{(2)}$ is adsorbed on top of the original surface or interface with $\chi^{(2)}$, the resultant susceptibility $\chi'^{(2)}$ can be theoretically described as

$$\chi'^{(2)} = \chi^{(2)} + \chi_{\Lambda}^{(2)} + \Delta\chi_I^{(2)} \quad (1.38)$$

where $\Delta\chi_I^{(2)}$ is the susceptibility changing as a result of any interaction owing to the adsorption process.²⁶

Therefore, by determining values of susceptibilities, SHG measurements can work in a remote-sensing way to characterize properties of the surface or interface, involving adsorption strength, surface coverage and symmetry, molecular orientation and interfacial electric strength etc. If the time resolution of excited laser pulses is sub-picosecond or femtosecond, it is also possible to achieve a dynamic observation process.

Second harmonic imaging microscopy

Since 1980s, SHG has become well implemented in nonlinear optical microscopy,²⁷ which can be used as a tool for materials diagnosis²⁸.

Second harmonic imaging microscopy²⁹ is based on SHG, where the second-order polarization oriented by the external optical field can generate coherent double-frequency light. So second harmonic imaging microscopy is regarded as a coherent imaging process,

which is highly directional with a high resolution. Because second harmonic signals are primarily from materials themselves, it is quite convenient to study biological structures like collagens without undermining biological functions. Therefore, second harmonic imaging microscopy is a breakthrough compared with linear optical microscopy.

1.3 Surface Plasmons Assisted Second Harmonic Generation

Surface plasmons (SPs) are waves that propagate along the surface of a metal. By altering the structure of metal's surface, the propagation of SPs can also change. In this section, propagation results of SPs on a planar surface and localized surface plasmons, which are confined to nanostructured surfaces, are briefly presented based on electromagnetic theories without detailed mathematical descriptions.

1.3.1 Background

SPs are collective oscillations of electrons on a metal surface.³⁰ Between 1902 and 1912, Wood first noticed that, when he shone polarized light on a metallic diffraction grating, a pattern of unusual dark and light bands appeared in the reflected light.^{31,32} In the fifties, Pines and Bohm suggested that the energy losses of fast electrons passing through metal foils is due to the excitation of conducting electrons and the creation of plasmons, which was a great step forward.³³ A complete explanation of SPs was not possible until 1968, when Otto, Kretschmann and Raether established a convenient method for the excitation of SPs.^{34,35} Since then, there has been a significant advance in both theoretical and experimental investigations of SPs.

Renewed interest in SPs has come from electromagnetic properties of nanostructured materials, which introduces the study of localized SPs.³⁶ The study of localized SPs started in the early 20th century, when Mie first explained the surprising optical properties of metallic colloids.³⁷ But further exploitation was limited by the capabilities to synthesize and manipulate nanoparticles in a controlled way. Till the development of nanotechnology at the end of 20th century, the applications of localized SPs spread quickly in different fields.

1.3.2 Electromagnetic explanation of plasmons

1.3.2.1 Planar surface plasmons

SPs are coherent oscillations of conduction electrons present at the interface of two media, associated with an electric field propagating along the interface. For SPs propagating on a planar surface, one example of classical structures is the dielectric-metal interface.

Figure 1.5 A dielectric-metal structure

As shown in Figure 1.5, a planar interface ($x=0$) is perpendicular to the x -axis, separating the dielectric and metal that are infinitely wide along the y -axis. Considering

an electromagnetic mode propagating along the interface in z direction, it can be regarded as a transverse electric (TE) or transverse magnetic (TM) mode. For wave propagation in the plane of interface which is yz , TE mode means the electric field is perpendicular to the propagation direction, while TM mode means the magnetic field is perpendicular to the propagation direction.³⁸

Assuming that the medium is linear isotropic and non-magnetic, based on the source-free Maxwell's equations (1.5)-(1.8), the wavevector equations can be written as

$$\begin{aligned}\Delta \mathbf{E} - \varepsilon \mu_0 \frac{\partial^2}{\partial t^2} \mathbf{E} &= \nabla (\mathbf{E} \cdot \nabla \ln \varepsilon) \\ \Delta \mathbf{H} - \varepsilon \mu_0 \frac{\partial^2}{\partial t^2} \mathbf{H} &= (\nabla \times \mathbf{H}) \times (\nabla \ln \varepsilon)\end{aligned}\tag{1.39}$$

By orienting Cartesian axes in Figure 1.5, field vectors depend on x and z directions only. Subject to the requirements that fields are bounded, equation (1.40) becomes

$$TE \text{ mode: } \frac{\partial^2 E_y(x)}{\partial x^2} + (\omega^2 \varepsilon \mu_0 - \beta^2) E_y(x) = 0, E_z = 0\tag{1.40}$$

$$TM \text{ mode: } \frac{\partial^2 H_y(x)}{\partial x^2} + (\omega^2 \varepsilon \mu_0 - \beta^2) H_y(x) = 0, H_z = 0\tag{1.41}$$

where ω is the frequency of electromagnetic wave and β represents the propagation constant.³⁹

Restricted by the boundary conditions of Maxwell's equations, it has been proved that equation (1.41) has no valid solution.³⁹ Therefore, there is a conclusion that only TM

mode can exist in SPs or only a p-polarized incident light is possible to be converted into SPs. Equation (1.42) gives the expression of β as

$$\beta = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} = k \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (1.42)$$

where c is the speed of light in vacuum, k is the free-space wave vector, and ϵ_i is the relative dielectric constant, where i represents m (metal) or d (dielectric).

For a lossless metal of Drude model, the dielectric constant is

$$\begin{aligned} \epsilon_m &= 1 - \frac{\omega_p^2}{\omega^2} \\ \omega_p &= \sqrt{4\pi n e^2 / m_0} \end{aligned} \quad (1.43)$$

where n is the density of electrons and m_0 is the mass of an electron. Substituting equation (1.44) into (1.43), we have

$$\beta^2 = \frac{\omega^2}{c^2} \frac{\epsilon_d (1 - \omega_p^2 / \omega^2)}{\epsilon_d + 1 - \omega_p^2 / \omega^2} \quad (1.44)$$

which describes the dispersion relation for SPs. When $\beta \rightarrow \infty$, there is

$$\omega = \frac{\omega_p}{\sqrt{1 + \epsilon_d}} \quad (1.45)$$

which is the frequency of SPs propagating on the dielectric-metal interface.³⁶

In order to excite SPs by p-polarized light, which is incident on a planar metal surface from the adjacent dielectric medium, the frequency of the incident light must equal that of SPs. However, we have

$$\beta = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \cong \sqrt{\frac{1}{1 - \frac{\epsilon_d}{\epsilon_m}}} \left(\frac{\omega \sqrt{\epsilon_d}}{c} \right) > \frac{\omega \sqrt{\epsilon_d}}{c} = k_{inc} \quad (1.46)$$

where k_{inc} is the wavevector of the incident light. Equation (1.48) indicates that the wavevector of SPs is larger than that of the incident light with the same frequency. Thus, light illuminating a metal surface through the medium cannot be directly coupled into SPs.⁴⁰ The incident light requires additional wavevector Δk_z in the plane of the surface to convert the energy of incident photons into SPs, as shown in Figure 1.6.

Figure 1.6 The coupling condition of wavevectors

$$\beta = k_{inc} \sin \theta \pm \Delta k_z \quad (1.47)$$

where θ is the angle of the incidence.

Therefore, special experimental approaches are needed to satisfy equation (1.49), such as prism coupling, grating coupling and so on.^{30,39}

1.3.2.2 Localized surface plasmons

In addition to SPs at a planar dielectric-metal interface, localized surface electromagnetic excitations can exist in other geometries, such as metallic nanoparticles. This is referred as localized surface plasmons. In this section, localized SPs of ideally spherical nanoparticles are briefly discussed by neglecting the spatial dependence.⁴⁰

In the quasi-static limit, electric field can be represented by a potential which satisfies the Laplace equations.

$$\begin{aligned}\mathbf{E} &= -\nabla\Phi \\ \nabla^2\Phi &= 0\end{aligned}\tag{1.48}$$

In spherical coordinates (r, θ, φ) , equation (1.50) can be expressed as⁴¹

$$\frac{1}{r^2 \sin \theta} \left[\sin \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \varphi^2} \right] \Phi(r, \theta, \varphi) = 0 \tag{1.49}$$

In the case of a metallic sphere with radius R and dielectric constant ε_m , which is centered at the origin and embedded in a medium of dielectric constant ε_d . The solution of equation (1.51) for the electrostatic potential can be written in the following form.

$$\begin{aligned}\Phi_1(r, \theta, \varphi) &= \sum_{\ell=0}^{\infty} \sum_{n=-\ell}^{\ell} A_{\ell n} r^{\ell} Y_{\ell n}(\theta, \varphi), 0 \leq r \leq R \\ \Phi_2(r, \theta, \varphi) &= \sum_{\ell=0}^{\infty} \sum_{n=-\ell}^{\ell} B_{\ell n} r^{-\ell-1} Y_{\ell n}(\theta, \varphi), r \geq R\end{aligned}\tag{1.50}$$

where $Y_{\ell n}(\theta, \varphi)$ is a spherical harmonic, $A_{\ell n}$ and $B_{\ell n}$ are constant coefficients to be determined by boundary conditions. According to the continuity of the tangential electric

fields and the normal components of electric displacements at the surface of the sphere, there are

$$\begin{aligned} \left(\frac{\partial\Phi_1}{\partial\theta}\right)_{r=R} &= \left(\frac{\partial\Phi_2}{\partial\theta}\right)_{r=R} \\ \varepsilon_m \left(\frac{\partial\Phi_1}{\partial r}\right)_{r=R} &= \varepsilon_d \left(\frac{\partial\Phi_2}{\partial r}\right)_{r=R} \end{aligned} \quad (1.51)$$

Thus, we have

$$A_{\ell n} = R^{-(2\ell+1)} B_{\ell n} \quad (1.52)$$

$$\varepsilon_m A_{\ell n} = -\left(\frac{\ell+1}{\ell}\right) \varepsilon_d R^{-(2\ell+1)} B_{\ell n} \quad (1.53)$$

Comparing equation (1.54) with (1.55) to eliminate $A_{\ell n}$ and $B_{\ell n}$, the result yields the dispersion relation for the frequencies of localized SPs.

$$\frac{\varepsilon_m}{\varepsilon_d} = -\frac{\ell+1}{\ell} \quad (1.54)$$

For a lossless metal under the Drude model, the frequency solution is

$$\omega_{np} = \sqrt{\frac{\ell}{\ell + (\ell+1)\varepsilon_d}} \omega_p \quad (1.55)$$

where ω_{np} is the frequency of localized SPs and ℓ is the multipole order.

The frequency of localized SPs is related to both the media and the particle size. If spheres are very small, only the dipole-active excitation ($\ell=1$) is important. In the limit of a very large sphere, where $\ell \rightarrow \infty$, ω_{np} approaches $\omega_p / \sqrt{\varepsilon_d + 1}$, which is the same than

the frequency of SPs in equation (1.47). Therefore, localized SPs can be possibly converted into SPs and can be excited by SPs in turn when the planar interface becomes rough enough.

1.3.3 Surface plasmon resonance

In 1908, G. Mie first used Maxwell's electromagnetic theory with proper boundary conditions to simulate the colorful effects of gold nanoparticles and concludes that the color changes with the diameter of gold spheres.⁴² This computation is referred as the Mie theory, which was interpreted in the surface plasmon resonance (SPR).

SPR occurs at the resonance frequency ω_{np} of SPs mentioned in section 1.3.2. Figure 1.7 is a good explanation by taking SPs of metallic nanoparticles as an example, which shows that at the resonance frequency, metal spheres absorb the incident light and generate the delocalization or polarization of electrons. As a result, electron waves are formed to oscillate around the surface, which are regarded as plasmons.

Figure 1.7 Delocalization of electrons in SPR⁴³

Hence, an appropriate frequency of light is needed to excite SPs. Experimentally, by examining the absorption spectra of metallic nanoparticles, a huge absorbance appears at

the wavelength of SPR, which is consistent with the resonance frequency. Also, the wavelength of SPR may shift to different optical frequencies, where different dielectric constants of materials would dominate changes in the refractive index.⁴⁴

1.3.4 Role of surface plasmons in second harmonic generation

As we know, SHG is forbidden in centrosymmetric structures. However, for a random distribution of nanostructures, the centrosymmetry is likely to be broken and SHG becomes electric-dipole allowed.⁴⁵ Through plasmonic effects like SPs of metallic nanoparticles, an effectively increased SHG can be achieved.

In 1981, A. Wokaun first observed surface-enhanced nonlinear optical effects and surface-enhanced Raman scattering (SERS) from roughened metal surfaces, which demonstrated that the incident electromagnetic field E_0 is modified into E_{in} inside metallic nanoparticles by the following relation.⁴⁶

$$E_{in} = f(\omega)E_0 \quad (1.56)$$

where $f(\omega)$ is defined as the local field enhancement factor of SPs. Local field factor represents the ratio of second harmonic intensity from a rough surface to that of a smooth surface.⁴⁷ As a result, the incident field is concentrated into a local field of small volumes through SPR.

As SHG requires an intense electromagnetic energy, local field enhancement plays an important role in enhancing the process of SHG. By examining SHG of silver island

film (SIF), A. Wokaun presented SPs assisted SHG, which was measured at a fundamental wavelength of 1064nm.⁴⁶

Figure 1.8 SHG from SIF as a function of mass thickness that is thickness measured by Quartz monitor in a vacuum chamber. (a) SHG excited at 1.06 μm , (b) Local field factor at 1.06 μm and 0.53 μm .⁴⁶

Figure 1.8 indicates that the maximum SHG was detected at a thinner thickness, which corresponds to the maximum range of local field factor at second harmonic frequency. Also, the maximum of local field factor shifts to the UV region for thinner films.⁴⁸ Y. R. Shen further calculated local field factor for other materials.⁴⁷

It was also concluded by A. Wokaun that second harmonic intensity $I_{(2\omega)}$ is proportional to the squared fundamental intensity $I_{(\omega)}^2$ in the case of metallic nanoparticles.⁴⁹

$$I_{(2\omega)} \propto f_{(\omega)}^4 f_{(2\omega)}^2 I_{(\omega)}^2 \quad (1.57)$$

where $f_{(\omega)}$ is local field factor at the fundamental frequency and $f_{2\omega}$ is local field factor at second harmonic frequency. Local field factor, which originates from the excitation of plasmons, proves that SHG is sensitive to the local field resonance.⁵⁰

Therefore, taking the advantage of plasmons, SHG is possible to be achieved with a reduced power. Till now, SHG assisted by plasmons has been investigated on metallic nanoparticles⁵¹, metal island film⁴⁸ and metal surfaces⁵², where the second order process is influenced by the roughness of surfaces and the shape or size of metallic nanoparticles.

On the other hand, SPs in the nanoscale allow the development of integrated photonic devices. Also, plasmonic excitations in the nonlinear optical effects only take a few femtoseconds, which increase the possibility of ultrafast optical signal processing technique. Although basic investigations of plasmons assisted nonlinear processes have been studied for decades, including the innovation of nanostructure fabrication, nonlinear plasmonics are still highly expected to move towards the future applications in nanophotonics.⁵³

1.4 Chiral Second Harmonic Generation

1.4.1 Chirality and linear optical activity

Chirality, also known as right or left handedness, occurs in a pair of enantiomers, as a consequence of lacking mirror-symmetry. Depending on the symmetry property, materials can be determined as chiral or achiral. Chiral materials widely exist in human

life, where the majority of biological molecules or compounds are chiral. This phenomenon was realized by scientists about one century ago. For example, all amino acids in proteins, sugars of DNA or RNA, and most of other bio-molecules come in one form of enantiomers. Therefore, chirality is subject to intense research, especially for pharmacology, medicinal and synthetic chemistry.⁵⁴

On the other hand, due to the natural optical activity, chiral materials can rotate the polarization plane of an incident beam clockwise or counterclockwise, which is termed as the optical rotation as shown in Figure 1.9. Hence, chiral materials can be further named as dextrorotatory (+) or levorotatory (-).

Figure 1.9 Schematic diagram of optical rotation⁵⁴

Optical rotation in chiral molecules was first discovered by J. B. Biot, in 1815. In 1822, a fundamental explanation to this phenomenon was given by A. Fresnel, where a linearly polarized light was considered as a vector sum of left and right circularly polarized light. In an optical-active chiral medium, the refractive indices are slightly different for a left and right circularly polarization light, which is known as the circular birefringence described as below.^{54,55}

$$\phi = \frac{2\pi}{\lambda} |n_L - n_R| \quad (1.58)$$

where ϕ in radians is the optical rotation, λ is the wavelength, and $|n_L - n_R|$ is the absolute difference of refractive index caused by left and right circularly polarized light.

Thus, a phase shift appears between left and right circular components owing to different travelling speeds, and manifests a rotation of linear polarization.⁵⁴ By measuring the optical rotation as a function of wavelength, optical rotatory dispersion spectra can be achieved. Also, the extent of optical rotation significantly depends on the concentration and length of chiral medium.

Another important phenomenon of linear optical activity is called circular dichroism, where chiral materials have a different absorbance ΔA between left and right circularly polarized light.⁵⁶

$$\Delta A = A_L - A_R \quad (1.59)$$

where A_L and A_R represent the absorbance of left and right circular polarization.

Unlike optical rotatory dispersion, circular dichroism only occurs at specific wavelengths. Circular dichroism measured as a function of wavelength is termed as circular dichroism spectroscopy. Hence, both optical rotatory dispersion and circular dichroism can be used to analyze optical information of chiral molecules.

1.4.2 Nonlinear optical activity: second harmonic generation

Because of the noncentrosymmetric structures of chiral materials, there is also a growing interest for their nonlinear optical responses. In this section, SHG of chiral molecules is briefly introduced.

As described in section 1.2.1, achiral materials are regarded as $C_{\infty v}$ symmetry, while chiral materials belong to C_∞ symmetry. Comparing equations (1.36) (1.37) (1.38) with (1.30) (1.31) (1.32), second-order susceptibility elements with “XYZ” are proved to be a probe of molecular chirality, which contributes to additional scalar components of second harmonic polarization as the following.

$$\begin{aligned}P_X^{Chiral}(2\omega) &= 2\varepsilon_0\chi_{XYZ}^{(2)}E_Y(\omega)E_Z(\omega), \\P_Y^{Chiral}(2\omega) &= 2\varepsilon_0\chi_{YZX}^{(2)}E_X(\omega)E_Z(\omega), \\P_Z^{Chiral}(2\omega) &= 2\varepsilon_0\chi_{ZXY}^{(2)}E_X(\omega)E_Y(\omega).\end{aligned}\tag{1.60}$$

Due to the contribution of chiral tensors $\chi_{XYZ}^{(2)}$, $\chi_{YZX}^{(2)}$, and $\chi_{ZXY}^{(2)}$, there is an optical rotation in the plane of second harmonic polarization. For a pair of chiral enantiomers, the sign of chiral tensors are opposite owing to their non-mirror symmetry chiral structures.⁵⁷

Experimentally, this effect has been detected through SHG-ORD (optical rotator difference) and SHG-CD (circular difference).

Figure 1.10 Polarization analyzed SHG signal from air/water interface for saturated aqueous solutions. The samples are R-BN (a), S-BN (b) and a 50:50 racemic mixture of R and S-BN (c). Second harmonic wavelength=301.5nm.⁵⁸

As shown in Figure 1.10, the idea of SHG-ORD is to excite chiral materials with a linearly polarized fundamental beam and measure the difference for any rotated linear polarization of second harmonic signal.⁵⁹ J. D. Byers et al. examined SHG-ORD for a pair of R- and S-enantiomers of 2, 2'-dihydroxy-1, 1' binaphthyl (BN), where the incident angle is fixed and second harmonic signals are analyzed. In Figure 1.10 (a) and (b), R- and S- enantiomers exhibit rotation angles ϕ of opposite sign at either $+17^\circ$ or -17° , yet

with the same magnitude. This comparison is a proof of reversed chiral tensors between R- and S-enantiomers. However, for the racemic mixtures of R- and S-enantiomers, the rotation angle is zero, which indicates that chiral tensors of the second-order susceptibility vanish.⁵⁹

Similarly, if the fundamental beam is chosen to be either left or right circularly polarized, the resultant difference at a linearly polarized second harmonic beam is called SHG-CD. F. Hache et al. presented SHG-CD of a pair of (+) and (-) enantiomers from the surface of Tröger's base by rotating a quarter waveplate, where second harmonic polarization is linearly analyzed. As shown in Figure 1.11, arrows at $+45^\circ$ and -135° represent the right circular polarization of the fundamental laser beam, while arrows at -45° and $+135^\circ$ represent the left circular polarization.⁶⁰

Figure 1.11 SHG-CD: p-polarized component of SHG signal as a function of the rotation angle of a quarter waveplate. Top: (+)-enantiomer; bottom: (-)-enantiomer.

In Figure 1.11, (+)-enantiomer exhibits a higher second harmonic intensity excited by left circularly polarized light than right circularly polarized light, while (-)-enantiomer exhibits a lower second harmonic intensity excited by left circularly polarized light than right circularly polarized light. The intensity difference of SHG between the incidence of left and right circular polarization is the same for each enantiomer. Obviously, SHG-CD of a pair of enantiomers responds oppositely to left and right circularly polarized light, which is also a verification of chirality.

Compared with the linear optical detection of optical rotator dispersion and circular dichroism, second harmonic intensity differences of chiral molecules measured in SHG-ORD and SHG-CD have been observed to be more obvious, where the electric-dipole approximation, even the magnetic dipolar and electric quadrupolar contributions are considered for chiral molecules.⁶⁰

Based on the examples above, it can be concluded that SHG-ORD and SHG-CD measurements are both efficient methods to reveal the handedness of a chiral molecule. Therefore, chiral SHG is a sensitive technique to be applied in the nonlinear chiral spectroscopies.

1.5 Research Motivation and Outline

In Chapter 1, background and basic theories of nonlinear optics, especially SHG, which includes SPs assisted SHG and chiral SHG, are briefly summarized. Various approaches for the optical detection of chiral compounds have been developed due to their natural optical activity. Since the advantages of SHG on noble metallic

nanoparticles have been observed, it would be interesting to study the nonlinear phenomena from chiral compounds attached metallic nanoparticles.

In the present work, I fabricated chiral-modified silver nanoparticles (Ag NPs) based on the self-assembly process of cysteine and silver, and carried out the investigation of SHG on modified and unmodified Ag NPs. For chiral-modified Ag NPs, either L-Cysteine (L-C) or D-Cysteine (D-C), as a pair of enantiomers, was applied on top of the Ag NPs.

I started my master program research with the fabrication of Ag NPs in a physical deposition way, where Ag NPs controlled under different deposition thickness are characterized with absorption spectra and AFM. Detailed descriptions of fabrication procedures, including the chiral modification process, will be presented in Chapter 2.

Following in Chapter 3, our experimental set-up of SHG measurements is introduced and SHG of unmodified Ag NPs is first discussed as a reference. Then a comparison of SHG-ORD of chiral-modified Ag NPs are analyzed between L-C/Ag NPs and D-C/Ag NPs, where the rotatory polarization of second harmonic signal is chosen at linearly $\pm 45^\circ$. SHG-CD is also observed. To identify whether SHG-ORD is influenced by the ratio changing between L-Cysteine and D-Cysteine, a series of mixture of L-Cysteine and D-Cysteine are applied on top of Ag NPs, where SHG-ORD are only measured at the maximum second harmonic intensity.

As chiral and achiral materials exhibit different second-order susceptibilities, calculation methods of second-order susceptibilities will be further introduced and a

theoretical interpretation to our experimental results will be accordingly discussed in Chapter 4.

However, looking forward to applying SHG in the diagnostics of cysteine as an optical sensor, there are still many promising plans unfinished due to limited master program. Future work will be briefly introduced in the Chapter 5.

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Chapter 2

Chiral-Modified Silver Nanoparticles

2.1 Synthesis of Silver Nanoparticles

2.1.1 Background

Synthesis of Ag NPs can be classified into two routes. One is the physical approach, including physical vapor deposition, laser ablation technique and so on. The other is the chemical approach, typically known as the chemical reduction or electrochemical deposition of metallic nanoparticles.^{1,2} During the chemical reduction, appropriate reductants and protective agents are both very important to control and stabilize nanoparticles, where choices of materials are accordingly limited.¹ For the electrolysis reaction, the uniformity and densities of nanoparticles can be influenced a lot by different controlling conditions.² Comparably, a physical approach, such as physical vapor deposition, has advantages of easy deposition monitoring and depositing many inorganic and organic materials without pollution.³

Since 1980, physical vapor deposition has been evolved based on the previous work.⁴ This deposition process was studied to deposit films of metal, compound and organic materials, where atoms or molecules surrounded by a vacuum or low-pressure gas are vaporized from the source and condensed on the surface of substrates. Based on varied vaporization ways and deposition environment, physical vapor deposition can be

categorized as vacuum evaporation, sputter deposition, arc vapor deposition, ion plating, and ion beam assisted deposition etc.⁵

In this study, Ag NPs, presented in the form of SIF,⁶ was deposited by means of vacuum thermal evaporation, where high-purity films can be deposited from high-purity source material directly⁷.

2.1.2 Vacuum thermal evaporation

Silver with 99.99% purity from Goodfellow is deposited on top of glass substrates. Glass substrates are commercial microscope slides with a thickness of 1mm from Fisherbrand, which were cut into a size of 2cm×2.5cm. Before deposition, glass plates were cleaned in an ultrasonic cleaner, sequentially with ethanol, isopropanol, acetone, and distilled water, and then, dried with nitrogen and in an oven at 100 ° for 10 minutes.

Figure 2.1 Principle components of Kurt J. Lesker thin film deposition system.

1-deposition thickness sensor, 2-substrate holder, 3-substrate,
4-substrate shutter, 5-deposition rate sensor, 6-source boat.

As shown in Figure 2.1, standard vacuum thermal evaporation in our system consists of three main steps: pump down, deposition and PC vent. Deposition process is run under a $<10^{-6}$ mbar (1Torr=1mm Hg=1.333mbar) vacuum chamber, which is supplied by a roughing pump and a turbo pump. Silver in the source boat is heated by Joule effect and evaporated into the vacuum.⁷ As glass substrates are fixed in a 180° face-down position, particulates won't settle on the surface, which provides a uniform deposition over the substrate surface.⁵ Because the evaporated vapor cools rapidly in the vacuum, it is possible to synthesis nanoparticles in a high concentration.¹ Both the deposition rate and thickness are detected by sensors, while the deposition time is counted by opening and closing the substrate shutter. At the same time, deposition process are precisely controlled

and recorded by the Sigma software.⁷ Nitrogen is used to vent the chamber back to the atmospheric pressure. Samples are stored at room temperature in a glove box.

Therefore, all of the synthesis procedures above are aiming to guarantee the stability and uniformity of growing Ag NPs without oxidation or impurities.

2.2 Characterization of Silver Nanoparticles

Ultraviolet-Visible (UV-Vis) spectrometer, Infrared (IR) spectrometer and Atomic force microscopy (AFM) were used to characterize Ag NPs. Because SHG of Ag NPs is strongly motivated at the wavelength of SPR,^{8,9} it is necessary to investigate the absorption properties of Ag NPs. In the deposition process of vacuum thermal evaporation, an average rate of 1.5-2.0 Å/s was used to fabricate Ag NPs controlled under different deposition thicknesses, where the thickness read by sensors are regarded as mass thickness. To avoid a continuously even silver thin film and to have a measurable comparison, deposition thickness was controlled approximately at 3nm, 5nm, 7nm, 9nm, 11nm, 13nm, 15nm, 17nm, 19nm with an deviation around 0.2nm. In this section, SIF under different deposition thickness are comparably characterized, in order to identify the origin of SHG in our experiments which will be discussed in Chapter 3. Fabrication methods and detailed discussions on morphologies of Ag NPs have been studied by previous researchers,^{10,11,12} which will not be further studied here.

2.2.1 Atomic force microscopy

AFM images were collected with Ambios Technology Q-Scope Scanning Microscope operated in the Wavemode (intermittent-contact mode) with a silicon tip from NanoAndMore, for a non-contact high frequency scanning.

Results and discussion

Figure 2.2 Three-dimensional AFM images of SIF under different deposition thicknesses

As shown in Figure 2.2, a surface of SIF was successfully formed on glass substrates due to the island-like growth of silver,¹³ when the deposition thickness is in the range of 3-19nm. To quantify the comparison of AFM images, surface roughness of each sample was measured with Gwyddion program and plotted in a relation of deposition thickness. The average roughness R_a is defined as the mean value of the surface height $\bar{Z}$ relative to the center plane, which is determined by the following equation.

$$R_a = \sum_{n=1}^N \frac{|Z_n - \bar{Z}|}{N} \quad (2.1)$$

where N is the number of points in the sample area.¹⁴ Average particle height is

$$\bar{Z} = \frac{1}{N} \sum_{n=1}^N Z_n \quad (2.2)$$

Figure 2.3 Average surface roughness of SIF under different deposition thicknesses. Error bars are ± 1 nm.

In Figure 2.3, surface roughness gradually decreases with an increased deposition thickness. Particle size was compared by measuring the average height of Ag NPs, as lateral dimensions may be easily distorted by tip convolution effects.¹⁵

Figure 2.4 Average particle size of Ag NPs under different deposition thicknesses. Error bars are ± 0.5 nm.

In Figure 2.4, particle size is raised by growing a larger deposition thickness. It may be owing to an aggregation of Ag NPs when the thickness is increased, which can also be seen in Figure 2.2 for some crystallization or island structures and a flatter surface roughness of SIF in Figure 2.3. Inter-particle distances for different SIF samples are similarly around 200 ± 10 nm and particle densities are similarly around 400 particles per $30 \mu\text{m}^2$. Error bars are deviations from several measurements.

2.2.2 Ultraviolet-Visible spectra

UV-Vis spectrophotometer (HP HEWLETT PACKARD DIODE ARRAY 8452A) was used to scan samples from 300nm to 800nm wavelength, where an empty glass substrate was tested as the baseline.

Results and discussion

Figure 2.5 UV-Vis absorption spectra comparison of SIF under different deposition thicknesses

In Figure 2.5, maximum absorbance of SIF has gradual red shift approximately from 440nm to 600nm. At the same time, an evident broadening of the absorption band and a growing tail appear for SIF with a deposition thickness larger than 13nm. These results can also be observed from the color changing of SIF.

Wavelength of SPR in each SIF was assigned to the wavelength with the maximum absorbance, which is due to collective oscillations from conduction electrons on the surface of Ag NPs.^{16,17} Thus, the wavelength of SPR shifts to a longer wavelength by increasing the deposition thickness. Further, examination of the wavelength of SPR dependent on particle size and surface roughness⁹ are observed in Figure 2.6, which indicates the wavelength of SPR increases with an increasing average particle size and decreases with an increasing SIF surface roughness. Error bars on wavelength of SPR represent deviations from several measurements.

Figure 2.6 Wavelength of SPR versus average particle size (left) or surface roughness (right) measured from AFM images as shown in Figure. 2.2. Error bars on wavelength of SPR are ± 5 nm.

It's known that the wavelength of SPR is in the UV range for isolated Ag NPs. However, in the form of SIF, Ag NPs are not isolated so that nanoparticles are possible to aggregate, where distortion of particle shape from sphere and dipole inter-particle interactions exist.⁶ Therefore, by raising deposition thickness, more and more Ag NPs may become electronically coupled, to form larger particles and lower the surface

roughness as a result of coherent islands. Those coupled Ag NPs present a red-shift in the wavelength of SPR than uncoupled Ag NPs. Generally, theoretical studies of localized surface plasmon resonance (LSPR) have predicted that a dipolar plasmon resonance is dominant at the red and a quadrupolar plasmon mode is dominant in blue.⁹ Detailed theoretical analyses are not introduced here. Our results also prove that UV-Vis is a method to monitor the behavior of nanoparticles.

2.2.3 Infrared spectra

IR spectra, as a complimentary comparison compared to UV-Vis spectra, were taken with Ocean Optics spectrometer with a scanned wavelength range from 800nm to 2400nm.

Results and discussion

Figure 2.7 IR absorption spectra comparison of SIF under different deposition thicknesses

Figure 2.7 indicates that SIF with a deposition thickness from 3nm to 11nm shows no absorbance in the IR region. However, for SIF with a deposition thickness larger than 13nm, there is a gradually increasing absorbance, which broadens from near-infrared to far-infrared. These interesting results may be also a result of aggregated or coupled Ag NPs, which would accordingly help illustrating the origin of SHG excited by an infrared laser described in Chapter 3.

2.3 Chiral Modification of Silver Nanoparticles

2.3.1 Chiral modified process

Chiral molecules used without further purification in this experiment are L-(+) Cysteine hydrochloride monohydrate (Abbreviated as L-Cysteine or L-C, CAS Number: 7048-04-6, Linear formula: $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH} \cdot \text{HCl} \cdot \text{H}_2\text{O}$) from J. T. Baker Chemical Co., and D-(-) Cysteine hydrochloride monohydrate (Abbreviated as D-Cysteine or D-C, CAS Number: 32443-99-5, Linear formula: $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH} \cdot \text{HCl} \cdot \text{H}_2\text{O}$) from Alfa Aesar. Ultrapure water (Millipore-Q) with a resistivity of 18 M Ω ·cm was used for solution preparation and rinsing.

Figure 2.8 Structures of L-Cysteine (left) and D-Cysteine (right)

As cysteine is a sulfur-containing amino acid as shown in Figure 2.8, chiral modification can be easily achieved through the formation of S-Ag coordination.¹⁸ The chiral modification process shown in Figure 2.9 is achieved by dipping a glass slide of Ag NPs into 1mM cysteine aqueous solution for 20 hours at room temperature. After sufficient self-assembly of S-Ag, sample slides were rinsed in ultrapure water several times to remove redundant solution on both sides of the substrate, and then dried with nitrogen. Therefore, cysteine is attached on top of Ag NPs to form chiral-modified Ag NPs, with a deeper color than unmodified Ag NPs observed.

Figure 2.9 Schematic chiral-modification process of Ag NPs

In our experiment, as only the density of Ag NPs can decide the total amount of chiral molecules attached, it makes no effect to change the concentration of cysteine solution. As L-Cysteine and D-Cysteine is a pair of enantiomers, in circular dichroism spectra, they should present reversed circular dichroism curves at the same wavelengths. This work has been done by previous workers¹⁹ and related data can be found in Appendix A. However, in our functionalized SIF, no signal of circular dichroism was detected.

2.3.2 Absorption spectra comparison

Figure 2.10 Absorption spectra comparison between modified and unmodified Ag NPs:
UV-Vis (left) and IR (right).

In Figure 2.10, it's obvious to see a broadening absorption band and a red shift in modified Ag NPs. This is owing to a larger refractive index of the surrounding material and disorder in the assembly.^{19,20} In IR, there is almost no difference between absorption spectra of modified and unmodified Ag NPs. But the shift of absorption band in UV-Vis has proved the successful chiral modification of Ag NPs.

2.4 Summary

In Chapter 2, synthesis procedures of Ag NPs and chiral modification of Ag NPs were introduced. During the deposition process, deposition thickness is the only condition adjusted within a reasonable and measurable range. We planned to measure SHG of different SIF samples and discussed related results in the next chapter, in order to find the origin of SHG in our experiment set-up. So characterization of each SIF,

including UV-Vis/IR spectra and AFM images, was monitored and gives consistent results.

AFM images of SIF present an increasing particle size and a decreasing surface roughness by increasing the deposition thickness. Both UV-Vis and IR spectra present a longer wavelength shift with an increasing thickness. All of these results, as a dependence of deposition thickness read by deposition system detectors, conclude that an aggregation and coupling among nanoparticles could change the morphology of surface and the wavelength of SPR. Absorption properties are very important in analyzing if SPR plays a role in the excitation of SHG.

The chiral modification process was described and easily achieved through the self-assembly between silver and cysteine. In our chiral-modified Ag NPs, no signal from circular dichroism was detected. Thus, by measuring the shift in UV-Vis absorption spectra between modified and unmodified Ag NPs, it finally verifies a successful fabrication of chiral-modified Ag NPs.

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Chapter 3

Experimental Second Harmonic Generation

3.1 Optical System and Signal Detection

3.1.1 Experimental set-up description

Figure 3.1 Schematic view of the set-up for SHG.

1-Optical chopper wheels, 2-Laser line filter centered at 1550nm ± 40nm, 3-Half waveplate at 1550nm, 4-Quarter waveplate at 1550nm, 5-“Beam focusing” lens group, consisting of a concave lens and two convex lenses, 6-Rotation platform, 7-Sample holder, 8-“Beam collecting” lens group, consisting of a convex lens and concave lens, 9-Equilateral dispersive prism, 10-Narrow band-pass filter centered at 780nm ± 30nm, 11-Linear polarizer, 12-Iris diaphragm, 13-Horizontal translation stage.

As shown in Figure 3.1, SHG was carried out with a Toptica FemtoFiber FFS diode pumped fiber laser at the fundamental wavelength of 1550nm, where the average intensity is $\bar{I}_\omega = 250mW$, emitting 100fs (1fs=10⁻¹⁵s) pulses in the repetition rate of f=90 MHz. The peak intensity $I_{peak}(\omega)$ in a single pulse can be calculated as:

$$I_{peak}(\omega) = \frac{\bar{I}_\omega}{f \Delta t} = \frac{250mW}{90MHz \times 100fs} \approx 2.8 \times 10^4 W \quad (3.1)$$

SHG was measured in transmission. The laser beam is linearly polarized and the direction of the linear polarization could be rotated using a half waveplate, or converted into a left or right circular polarization using a quarter waveplate. Incident laser beam was further focused into a minimum spot size. Figure 3.2 is a brief drawing of the Gaussian beam.

Figure 3.2 Schematic description of Gaussian beam.

According to the Rayleigh criterion¹, the Gaussian waist and Rayleigh range of a focused Gaussian beam can be estimated as

$$\omega_0 = \frac{1.22\lambda f}{D} \quad (3.2)$$

$$z_R = \frac{\pi\omega_0^2}{\lambda} \quad (3.3)$$

where $\lambda = 1550\text{nm}$ is the fundamental wavelength, $D = 4\text{mm}$ is the diameter of laser beam on the last convex lens, and $f = 3.81\text{cm}$ is the focal length of the last convex lens. As a result, the Gaussian waist is $\omega_0 = 18\mu\text{m}$ and the Rayleigh range is $2z_R = 0.32\text{mm}$. Thus, average power density $\bar{\rho}$ of the focused laser beam within the Rayleigh range is estimated as follows.

$$\bar{\rho} = \frac{\bar{I}_\omega}{A} \approx \frac{\bar{I}_\omega}{\pi\omega_0^2} = \frac{250\text{mW}}{\pi \times (18\mu\text{m})^2} \approx 2.46 \times 10^8 \text{W} / \text{m}^2 \quad (3.4)$$

Sample slide was mounted vertically onto a rotation platform to vary the incident angle θ , ranging from 0° to 60° . The central position of the sample slide can be adjusted through a horizontally transitional stage. The normal of the sample surface is in Z direction and the Cartesian coordinate system is applied accordingly. As the glass substrate used for silver deposition possesses a thickness of 1mm, which definitely exceeds the Rayleigh range, experimental errors should be considered depending on whether the laser is precisely focused on the silver interface.

In the detection part, second harmonic signal in transmission was filtered by an N-SF11 equilateral dispersive prism, optically selected by a narrow band-pass filter, collected by a photomultiplier tube (PMT, Hamamatsu) and recorded by a digital oscilloscope (Agilent Technologies DSO-X 2012A). Polarization of the second harmonic

signal was analyzed using a linear polarizer. Standard lock-in techniques², including a lock-in amplifier (Stanford Research Systems SR510) and a chopper system (Newport 75160) fixed at the highest frequency of 2000 Hz, are used to extract second harmonic signal from noise and enhance detection sensitivity.

3.1.2 PMT calibration

PMT is a detector which absorbs photons incident on the sensitive area and generates photoelectrons almost simultaneously. After the amplification by lock-in amplifier, the intensity of photons detected by PMT is directly read in the form of voltage in an arbitrary unit (a.u.) on the screen of oscilloscope. The relation for voltages read from oscilloscope and PMT can be expressed as:

$$V_{PMT} = \frac{V_{OSC} \times S_{LIA}}{10(V)} \quad (3.5)$$

where V_{PMT} is the voltage output of PMT, V_{OSC} is the average voltage read from oscilloscope, and S_{LIA} is the sensitivity chosen on lock-in amplifier.

Comparably, optical power meter can be used to read the intensity of photons in the form of power. However, for the detection of weak light signal, PMT has the advantage of highly sensitivity than the silicon detector. To quantify the magnitude of second harmonic intensity in the form of power in our experimental set-up, a simple comparison between PMT and the optical power meter is applied. First, an attenuated laser beam at 775 nm was used instead of 1550nm in the same experimental set-up. Second, photon

detection is distinguished by either PMT or an optical power meter (Newport 1916-C).

Thus, we roughly obtain a power-voltage conversion coefficient ζ of PMT expressed as:

$$\zeta = \frac{Power}{Voltage} \approx 43.3 \mu\text{W/V} \quad (3.6)$$

As the intensity of the incident beam is not as low as the detection limit of each detector, it is reasonable to use the method above, which would help the determination of the actual power of weak signals in future SHG experiments.

3.1.3 Definition of polarization directions

Figure 3.3 Schematic illustration of p- and s-polarization.

As shown in Figure 3.3, p- or s-polarization refers to the oscillating plane of electric field of the light beam. S-polarization is always perpendicular to the plane of incidence, while p-polarization is in the plane of incidence. With the calculated comparison between reflection and transmission, there is only s-polarized light in the reflection at Brewster angle, while both p- and s-polarized light exist in the transmission.³

Figure 3.4 Definition of polarization directions at p/s/ $\pm 45^\circ$ in our set-up.

For a linear polarizer as shown in Figure 3.4, p- and s-polarized light can be selected with a phase difference of 90° . Accordingly, 45° -polarized light is defined as a phase difference of 45° compared with p-polarization, with a distinguished sign of $\pm$.

A linearly polarized light can also be converted into a circularly polarized light, through a quarter waveplate. For a p-polarized light, the only requirement is an angle difference of 45° between the fast axis of the quarter waveplate and the p-polarization. Also, a right circular polarization refers to a clockwise rotation, and a left circular polarization refers to a counterclockwise rotation.⁴

3.2 SHG of Silver Nanoparticles

3.2.1 Experimental observations

In Chapter 2, we have fabricated a series of Ag NPs through controlling the deposition thickness, which presented varied absorption spectra and surface morphologies. Then we used SHG to investigate their nonlinear optical properties and

found out that only Ag NPs with a proper deposition thickness can be detected with certain intensity of second harmonic signals under our experimental conditions.

Figure 3.5 Possibility of SHG of Ag NPs under different deposition thicknesses.

Column value of “0” represents there is no SHG detected and “1” represents SHG can be detected.

As shown in Figure 3.5, for Ag NPs with a deposition thickness approximately from 3nm to 11nm, no SHG was detected. However, for Ag NPs with a deposition thickness around 13nm to 19nm, SHG can be detected in our experimental set-up. Considering the UV-Vis absorption comparison mentioned in Chapter 2, it has proved that the maximum absorbance shifts to a longer wavelength with an increased deposition thickness, where an obvious absorbance at second harmonic wavelength around 775nm starts to appear at a thickness larger than 13nm. Also, the IR absorption comparison shows that there is no absorbance for the deposition thickness from 3nm to 11nm, but there is an increasing absorbance especially around 1550nm when the deposition thickness is larger than 13nm. Therefore, based on our experimental results, the following two explanations to the origin of SHG of Ag NPs under different deposition thicknesses may be possible.

First, certain absorbance at 775nm is likely to enhance the intensity of SHG because of SPR of Ag NPs. For Ag NPs with a deposition thickness larger than 13nm, wavelength of SPR appears in the red region, which supports a concentrated generation of second harmonic signals in specific scattering directions.⁵ In another word, within the detection limitation of our experimental set-up, only SHG assisted by SPs could be observed. Thus, in our experiments, it is not easy to detect SHG for Ag NPs without SPR.

Second, intense electromagnetic field of the fundamental light, which could be confined around Ag NPs, is an essential requirement to excite SHG in our experiments. For Ag NPs with a deposition thickness larger than 13nm, absorption around 1550 nm indicates that there is a resonance of the fundamental light around the sample surface. This resonance would make the incident light strongly concentrated around Ag NPs. Here we didn't focus on studying the findings of this resonance. But it is an interesting result to prove that SHG could only be excited for Ag NPs fabricated with an absorbance at the fundamental wavelength.

3.2.2 Results and discussion

In this section, SHG is excited by a p-polarized fundamental light and second harmonic light is analyzed at p- and s-polarization.

Figure 3.6 SHG of Ag NPs analyzed at p- and s- output polarization. Error bars on SHG are ± 0.003 .

Figure 3.6 shows the incidence dependent SHG of Ag NPs, where both curves present a similar trend except a stronger second harmonic intensity in the p-polarization than s-polarization output. This result suggests that the output of second harmonic light is not as linearly polarized as the fundamental. Referred to the p-polarized fundamental, second harmonic signal should theoretically vanish at normal incidence. Because the polarization of incident electric field at this position is totally parallel to the sample surface, resulting in no electric dipole along the normal in Z direction of the sample surface. However, in Figure 3.6, there is a non-zero intensity at normal incidence. It may be caused by the unprecisely focused laser beam on the interface as mentioned in section 3.1.1, where the laser beam indeed diverges out of the Rayleigh range. So a weak electric field component in Z direction should exist. By increasing the incident angle, a stronger second harmonic intensity is expected owing to an increased projection of the laser

polarization to the normal of the surface. The weak modulation around 30° has been attributed to roughness or impurities on the surface.⁶ It could also be simply due to an interference of weak SHG emitted from the back surface of the glass substrate.⁷ After 40° , second harmonic intensity declines rapidly because of increasing reflection at second harmonic and decreasing transmission at second harmonic.

According to the power-voltage conversion coefficient ζ of PMT roughly calculated in section 3.1.2, second harmonic intensity at the maximum of each second harmonic curve for an incident angle around 30° in Figure 3.6 could be estimated. Experimentally, at each incident angle, average intensity of second harmonic is recorded.

At the maximum of p-polarized second harmonic curve, average intensity $\bar{I}_{2\omega}^p \approx 3.89nW$;

At the maximum of s-polarized second harmonic curve, average intensity $\bar{I}_{2\omega}^s \approx 1.73nW$.

Therefore, for SHG of Ag NPs excited by a p-polarized fundamental light, $\bar{I}_{2\omega}^p : \bar{I}_{2\omega}^s \approx 2.25$. Second harmonic conversion efficiency η can also be estimated using $\eta = \bar{I}_{2\omega} / \bar{I}_\omega \approx 10^{-9}W / 10^{-1}W = 10^{-8}$, which is the average intensity at second harmonic over the average intensity at the fundamental.

As concerns to peak intensities of second harmonic, by using equation (3.1), we could also calculate peak intensities for a single pulse.

At the maximum of p-polarized second harmonic curve, peak intensity

$$I_{peak}^p(2\omega) \approx 0.43mW ;$$

At the maximum of s-polarized second harmonic curve, peak intensity

$$\bar{I}_{peak}^s(2\omega) \approx 0.19mW .$$

Obviously, in our experiments, it is a rather weak SHG process, which is very difficult to be detected. Error bars on second harmonic intensity are estimated from the fluctuations of signals around the mean value.

3.3 SHG of Chiral-Modified Silver Nanoparticles

3.3.1 Experimental comparison with Ag NPs

Similar experiments on chiral-modified Ag NPs by either L-Cysteine or D-Cysteine are observed with a p-polarized fundamental light, where second harmonic light is also analyzed in both p- and s-polarization, as shown in Figure 3.7 and Figure 3.8.

Figure 3.7 SHG of L-C/Ag NPs analyzed at p- and s- output polarization. Error bars on SHG are ± 0.003 .

Figure 3.8 SHG of D-C/Ag NPs analyzed at p- and s- output polarization. Error bars on SHG are ± 0.003 .

Comparing Figure 3.6 with Figure 3.7 and Figure 3.8, chiral-modified Ag NPs present almost the same second harmonic curves, where the intensity of p-polarized second harmonic light is also higher than that of s-polarized second harmonic light, except small differences in θ_{MAX} , which is the incident angle referred to the maximum of second harmonic curves. For unmodified Ag NPs, $\theta_{MAX} \approx 30^\circ \pm 10^\circ$, while $\theta_{MAX} \approx 35^\circ \pm 5^\circ$ for L-C/Ag NPs and $\theta_{MAX} \approx 40^\circ \pm 5^\circ$ for D-C/Ag NPs. This may be due to a modified distribution of nanoparticles and varied nonlinear properties after the chiral modification process. In our experiments, the maximum intensity of SHG from each sample is not comparable, because samples for each SHG measurement are different and Ag NPs even controlled under the same deposition thickness cannot be exactly the same in their surface properties.

Similarly, at the maximum of each second harmonic curve, average intensity could be estimated.

For L-C/Ag NPs, we have $\bar{I}_{2\omega}^p \approx 3.90nW$ and $\bar{I}_{2\omega}^s \approx 1.73nW$, where $\bar{I}_{2\omega}^p : \bar{I}_{2\omega}^s \approx 2.25$ and $\eta \approx 10^{-8}$.

For D-C/Ag NPs, we have $\bar{I}_{2\omega}^p \approx 3.25nW$ and $\bar{I}_{2\omega}^s \approx 1.52nW$, where $\bar{I}_{2\omega}^p : \bar{I}_{2\omega}^s \approx 2.14$ and $\eta \approx 10^{-8}$.

Therefore, observations for SHG, which are excited by a p-fundamental light and analyzed at p- or s-polarized second harmonic, present almost no difference between unmodified and modified Ag NPs.

3.3.2 Results of SHG-ORD

In Chapter 1, a general idea of SHG-ORD was introduced, which is proved to be a method of probing chiral molecules. In our experiments, considering the weak conversion efficiency of SHG, we will detect SHG-ORD in a different way, where the fundamental light is fixed to p-polarization and second harmonic signals will be analyzed in the linear polarization at $\pm 45^\circ$ as defined in Figure 3.4.

Figure 3.9 SHG-ORD of Ag NPs. Error bars on SHG are ± 0.003 .

Figure 3.9 shows the result of SHG-ORD in unmodified Ag NPs. There is no difference between $+45^\circ$ and -45° output polarization, which indicates an equal second harmonic intensity between $\pm 45^\circ$ polarizations. Here, Figure 3.6 and Figure 3.9 are obtained with the same sample of Ag NPs. By comparing the intensity at the maximum of each second harmonic curve, we have $\bar{I}_{2\omega}^p > \bar{I}_{2\omega}^{+45^\circ} = \bar{I}_{2\omega}^{-45^\circ} > \bar{I}_{2\omega}^s$. A comparable plot

combining results of Figure 3.6 and Figure 3.9 can be found in Appendix B. Therefore, there is no optical rotatory difference in SHG of unmodified Ag NPs.

Figure 3.10 SHG-ORD of L-C/Ag NPs. Error bars on SHG are ± 0.003 .

Figure 3.11 SHG-ORD of D-C/Ag NPs. Error bars on SHG are ± 0.003 .

In Figure 3.10 and Figure 3.11, we see a similar trend with unmodified Ag NPs in the incidence dependent SHG in Figure 3.9. However, there is a net second harmonic difference between +45 ° and -45 ° output polarization, which is well outside of error bars in modified Ag NPs. Figure 3.10 shows that L-C/Ag NPs has a stronger second harmonic intensity at -45 ° polarization than at +45 ° polarization. Oppositely, we notice in Figure 3.11 that D-C/Ag NPs has a weaker second harmonic intensity at -45 ° polarization than at +45 ° polarization. Due to opposite chiral structures, in SHG-ORD, we see that the plane of second harmonic polarization is “reversely rotated” between L-C/Ag NPs and D-C/Ag NPs.

Figure 3.7 and Figure 3.10 were obtained with the same sample of L-C/Ag NPs, and Figure 3.8 and Figure 3.11 were obtained with the same sample of D-C/Ag NPs. By comparing the intensity at the maximum of each second harmonic curve, we have $\bar{I}_{2\omega}^p > \bar{I}_{2\omega}^{-45^\circ} > \bar{I}_{2\omega}^{+45^\circ} > \bar{I}_{2\omega}^s$ for L-C/Ag NPs and $\bar{I}_{2\omega}^p > \bar{I}_{2\omega}^{+45^\circ} > \bar{I}_{2\omega}^{-45^\circ} > \bar{I}_{2\omega}^s$ for D-C/Ag NPs, where comparable plots combining results of L-C/Ag NPs from Figure 3.7 and Figure 3.10 or results of D-C/Ag NPs from Figure 3.8 and Figure 3.11 could be found in Appendix B. These results indicate that chiral-modified Ag NPs have the ability to generate a rotated second harmonic polarization, where second harmonic intensities at $\pm 45^\circ$ polarizations are unequal.

Comparatively, Ag NPs alone show no optical rotation in Figure 3.9. Therefore, cysteine induces optical anisotropy in SHG of chiral-modified Ag NPs, owing to its chiral

structures. In another word, SHG-ORD probes the existence of chirality in chiral-modified Ag NPs.

3.3.3 Results of SHG-CD

SHG-CD introduced in Chapter 1 has also been proved as a method to probe chirality. In this thesis, SHG-CD is excited by either right circularly polarized or left circularly polarized fundamental light and second harmonic light is analyzed at p-polarization. Here we only present SHG-CD on chiral-modified Ag NPs as shown in Figure 3.12 and Figure 3.13, to offer complementary results for the existence of chirality in chiral-modified Ag NPs, which is induced by cysteine.

Figure 3.12 SHG-CD of L-C/Ag NPs. Error bars on SHG are ± 0.003 .

Figure 3.13 SHG-CD of D-C/Ag NPs. Error bars on SHG are ± 0.003 .

In Figure 3.12, L-C/Ag NPs exhibit a stronger second harmonic intensity excited at left circularly polarized light than at right circularly polarized light involving error bars. Oppositely, in Figure 3.13, D-C/Ag NPs exhibit a stronger second harmonic intensity excited at right circularly polarized light than at left circularly polarized light involving error bars. As mentioned in Chapter 2, L-Cysteine we used is a (+)-enantiomer and D-Cysteine is a (-)-enantiomer. Thus, our results correspond to Figure 1.11 in Chapter 1, which concludes that (+)-enantiomer exhibits a higher second harmonic intensity excited by left circularly polarized light than right circularly polarized light, while (-)-enantiomer exhibits a lower second harmonic intensity excited by left circularly polarized light than right circularly polarized light. However, our results are not ideal with such a big difference between the maximum second harmonic intensity excited by either right or left

circular polarization. This may be because we are detecting a layer of cysteine covered Ag NPs, which provides a nonlinear contribution from chirality.

This result indicates that there is also a reversed rotation of second harmonic polarization in SHG-CD of chiral-modified Ag NPs, which further supports the existence of reversed chirality between L-C/Ag NPs and D-C/Ag NPs observed in SHG-ORD.

3.3.4 Discussion

In Chapter 1, we have compared the difference of second-order nonlinear susceptibilities in achiral and chiral molecules. In our experiments, unmodified Ag NPs can be regarded as achiral with $C_{\infty v}$ symmetry, while cysteine is chiral with C_∞ symmetry. For $C_{\infty v}$ symmetry, $\chi^{(2)}$ is composed of elements with $\chi_{ZZX}^{(2)}$, $\chi_{ZYY}^{(2)}$, $\chi_{ZZZ}^{(2)}$ and $\chi_{XZX}^{(2)}$, when Kleinman symmetry holds. However, for C_∞ symmetry, additional elements with $\chi_{XYZ}^{(2)}$, $\chi_{YZX}^{(2)}$ and $\chi_{ZXY}^{(2)}$ exist only in chiral molecules deprived of mirror symmetry. They are zero in achiral materials. As L-Cysteine and D-Cysteine are a pair of enantiomers, they hold a reverse sign of the “XYZ” surface-susceptibility elements. The rotated second harmonic polarization observed in SHG-ORD or SHG-CD of L-C/Ag NPs and D-C/Ag NPs is a proof of the existence of the “XYZ” surface-susceptibility elements. Hence one of the “XYZ” surface-susceptibility elements allows probing the chirality through SHG. We can also conclude that the self-assembly chiral-modified process described in Chapter 2 is successful in keeping the chiral properties of cysteine after its attachment onto Ag NPs. Here we didn't further study the formation mechanism of the

chiral modification between silver and cysteine. A detailed calculation of second-order susceptibilities will be discussed in Chapter 4.

To further investigate the influences of chirality induced by L-Cysteine and D-Cysteine in SHG of chiral-modified Ag NPs, SHG-ORD measurements in the same way were conducted on a series of chiral-modified Ag NPs, where a mixture of L-Cysteine and D-Cysteine was attached onto Ag NPs. The concentration of the mixture is 1mM, where the ratio of D-Cysteine gradually varies from 0, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% to 100%.

Supposed that the maximum optical rotatory difference of SHG-ORD could be estimated by

$$\Delta_{ORD}^{MAX} = I_{2\omega}^{+45^\circ} - I_{2\omega}^{-45^\circ} \quad (3.7)$$

For each sample, we only measured the approximately maximum second harmonic intensity at the linearly output polarizations of $\pm 45^\circ$ by selecting a proper incident angle around $30^\circ \sim 40^\circ$.

Figure 3.14 Maximum difference of SHG-ORD versus the ratio of D-Cysteine in a mixture of L-Cysteine and D-Cysteine modified Ag NPs. Error bars on SHG are ± 0.001 . Solid line is the best linear fit to equation (3.8), $R^2=0.97$.

From Figure 3.14, it can be noticed that when the ratio of D-Cysteine is linearly decreasing or when the ratio of L-Cysteine is linearly increasing, the maximum difference of SHG-ORD is also linearly decreasing. The linear fitting equation is given by

$$\Delta_{ORD}^{MAX} = -0.002R_{D-C} + 0.01 \text{ or } \Delta_{ORD}^{MAX} = 0.002R_{L-C} + 0.008 \quad (3.8)$$

where R_{D-C} and R_{L-C} respectively represent the ratio of D-Cysteine and L-Cysteine in their mixture. After conversion into the form of power, there are $\Delta_{ORD}^{MAX} \approx 0.43nW$ for L-C/Ag NPs and $\Delta_{ORD}^{MAX} \approx 0.39nW$ for D-C/Ag NPs.

This result is a good observation of opposite chirality between L-C/Ag NPs and D-C/Ag NPs, which may further help proving the existence of a reverse sign of the “XYZ”

surface-susceptibility elements in chiral-modified Ag NPs induced by L-Cysteine and D-Cysteine.

3.4 Summary

In Chapter 3, a detailed description of the experimental set-up is introduced and proved to be capable of detecting second harmonic signals even in the scale of nW. From the observation of SHG of Ag NPs fabricated under different deposition thicknesses, we found that only Ag NPs with SPR in the red region and absorbance around the fundamental wavelength are able to generate second harmonic signals. However, SHG process in our experiments is rather weak. SHG of chiral-modified Ag NPs is comparably discussed with unmodified Ag NPs, where SHG-ORD and SHG-CD as introduced in Chapter 1 are conducted to investigate the existence of chirality in chiral-modified Ag NPs. A general discussion based on the different symmetry properties between achiral and chiral materials is given to explain the “reversely rotated” second harmonic polarization in chiral-modified Ag NPs. With a further investigation of opposite handedness between L-Cysteine and D-Cysteine, we could conclude that we have successfully induced chirality by attaching L-Cysteine or D-Cysteine onto Ag NPs and SHG of chiral-modified Ag NPs can be used as a diagnostic of chiral molecules.

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Chapter 4

Theoretical Interpretation of Second Harmonic Generation

4.1 Basic Theory

Figure 4.1 Geometry of transmitted SHG from a thin film corresponding to Figure 3.1, 3.3 and 3.4. The fundamental beam at frequency ω is incident at angle θ and second harmonic beam at frequency 2ω is transmitted at angle θ'' .

In Figure 4.1, let us consider that the sample is single-side Ag NPs on top of glass.

In our experiments, the thickness l_{Ag} of Ag NPs is around 15nm and the thickness l_{glass} of glass is 1mm. As $l_{Ag} \ll l_{glass}$, l_{Ag} can be regarded as zero.¹ Thus, it can be estimated that both the fundamental and second harmonic light are incident on the interface between silver and glass at angle θ and transmitted at angle θ' in glass. As the glass substrate is parallel between the top and bottom, the fundamental light would have a transmission at angle θ and second harmonic light has a transmission at angle θ'' due to a different wavelength. The transmission angle of second harmonic light is then given by

$$\sin \theta'' = \frac{n_{glass}^{2\omega}}{n_{glass}^{\omega}} \cdot \sin \theta \quad (4.1)$$

where n_{glass}^{ω} and $n_{glass}^{2\omega}$ are refractive index of glass at the fundamental and second harmonic wavelength.

From Figure 4.1, the **p-s** basis is related to the Cartesian vectors by²

$$\mathbf{p} = \cos \theta \mathbf{X} + \sin \theta \mathbf{Z}, \mathbf{s} = -\mathbf{Y} \quad (4.2)$$

So in **p-s** basis, the direction of any linear polarization **l** can be described by

$$\mathbf{l} = \sin \varphi \mathbf{p} + \cos \varphi \mathbf{s} = \sin \varphi \cos \theta \mathbf{X} + \sin \varphi \sin \theta \mathbf{Z} - \cos \varphi \mathbf{Y} \quad (4.3)$$

where φ is the tilt angle from s-polarization as shown in the left of Figure 4.2.

Figure 4.2 Coordinate system of **p-s** basis (left) and its relation with Cartesian coordinates (right).

The fundamental beam $\mathbf{E}(\omega)$ can be divided into p and s components as shown in the right of Figure 4.2.

$$\begin{aligned} \mathbf{E}(\omega) &= \mathbf{E}_p(\omega) + \mathbf{E}_s(\omega) = E(\omega) \sin \varphi \mathbf{p} - E(\omega) \cos \varphi \mathbf{s} \\ &= E(\omega) \sin \varphi \cos \theta \mathbf{X} + E(\omega) \sin \varphi \sin \theta \mathbf{Z} + E(\omega) \cos \varphi \mathbf{Y} \\ &= \mathbf{E}_x(\omega) + \mathbf{E}_y(\omega) + \mathbf{E}_z(\omega) \end{aligned} \quad (4.4)$$

Therefore, there are

$$E_x(\omega) = E_p(\omega) \cos \theta, E_y(\omega) = -E_s(\omega), E_z(\omega) = E_p(\omega) \sin \theta \quad (4.5)$$

As mentioned in Chapter 1, the second-order susceptibility can be written as

$$\chi^{(2)} = \begin{bmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & \chi_{xyz} & \chi_{xxz} & \chi_{xxy} \\ \chi_{yxx} & \chi_{yyy} & \chi_{yzz} & \chi_{yzy} & \chi_{yxz} & \chi_{yyx} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & \chi_{zyz} & \chi_{zxz} & \chi_{zxy} \end{bmatrix} \quad (4.6)$$

Second harmonic polarization described in the form of matrix is given by

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = \epsilon_0 \begin{bmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & \chi_{xyz} & \chi_{xxz} & \chi_{xxy} \\ \chi_{yxx} & \chi_{yyy} & \chi_{yzz} & \chi_{yzy} & \chi_{yxz} & \chi_{yyx} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & \chi_{zyz} & \chi_{zxz} & \chi_{zxy} \end{bmatrix} \begin{bmatrix} E_x(\omega)^2 \\ E_y(\omega)^2 \\ E_z(\omega)^2 \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{bmatrix} \quad (4.7)$$

and

$$\begin{aligned} E_x(\omega)^2 &= \cos^2 \theta E_p(\omega)^2 \\ E_y(\omega)^2 &= E_s(\omega)^2 \\ E_z(\omega)^2 &= \sin^2 \theta E_p(\omega)^2 \\ 2E_y(\omega)E_z(\omega) &= 2 \sin \theta E_s(\omega) E_p(\omega) \\ 2E_x(\omega)E_z(\omega) &= 2 \cos \theta \sin \theta E_p(\omega)^2 \\ 2E_x(\omega)E_y(\omega) &= 2 \cos \theta E_p(\omega) E_s(\omega) \end{aligned} \quad (4.8)$$

Thus, we have

$$|\mathbf{P}(2\omega)| \propto \epsilon_0 \chi_{eff}^{(2)} E_{p,s}(\omega)^2 f(\sin \theta, \cos \theta) \quad (4.9)$$

where $f(\theta)$ is a function of the incident angle.

In equation (4.9), reflectance loss of second harmonic light is not included, which is mainly caused by reflection at the silver/glass interface. According to Fresnel's equations, transmission coefficients are

$$\begin{aligned} t_s &= \frac{2n_{air} \cos \theta}{n_{air} \cos \theta + n_{glass}^{2\omega} \cos \theta'} \\ t_p &= \frac{2n_{air} \cos \theta}{n_{air} \cos \theta' + n_{glass}^{2\omega} \cos \theta} \end{aligned} \quad (4.10)$$

where t_s and t_p refer to s- and p-polarization respectively, and n_{air} is refractive index of air.

The transmittance factor for second harmonic light is then given by

$$T_{p,s} = \frac{n_{glass}^{2\omega} \cos \theta'}{n_{air} \cos \theta} t_{p,s}^2 \quad (4.11)$$

In Chapter 1, local field factor in SHG of metallic island film was mentioned due to local field effects.³ Local field factor is especially useful in comparing SHG from Ag NPs under different deposition thicknesses.⁴ In Chapter 3, experimental SHG were conducted on Ag NPs with a general deposition thickness around 15nm, so we will not involve this factor into the following calculations.

Therefore, second harmonic intensity, where $I(2\omega) \propto |\mathbf{P}(2\omega)|^2$, can be written as

$$I_{p,s}(2\omega) \approx T_{p,s} \left| \varepsilon_0 \chi_{eff}^{(2)} f(\sin \theta, \cos \theta) \right|^2 I_{p,s}(\omega)^2 \quad (4.12)$$

where the fundamental intensity $I_{p,s}(\omega) = \frac{c}{8\pi} E_{p,s}(\omega)^2$. Theoretical fitting of SHG

dependent with incidence can be roughly simulated according to equation (4.12).

4.2 Chiral and Achiral Second-Order Susceptibilities

In Chapter 3, chirality was observed in SHG of chiral-modified Ag NPs compared with unmodified Ag NPs. As mentioned in Chapter 1, there are additional second-order susceptibility elements in chiral materials than achiral materials. Therefore, for chiral-modified Ag NPs, $\chi^{(2)}$ may be regarded as two parts

$$\chi^{(2)} = \chi_{chiral}^{(2)} + \chi_{achiral}^{(2)} \quad (4.13)$$

where $\chi_{chiral}^{(2)}$ and $\chi_{achiral}^{(2)}$ represent chiral and achiral components respectively.

According to equation (4.7) and (4.8), second harmonic polarization for chiral-modified Ag NPs can be expressed as

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = \varepsilon_0 \begin{bmatrix} 2\chi_{xyz}^{(2)} E_y(\omega) E_z(\omega) + 2\chi_{xxz}^{(2)} E_x(\omega) E_z(\omega) \\ 2\chi_{yzy}^{(2)} E_y(\omega) E_z(\omega) + 2\chi_{yzx}^{(2)} E_x(\omega) E_z(\omega) \\ \chi_{zxx}^{(2)} E_x(\omega)^2 + \chi_{zyy}^{(2)} E_y(\omega)^2 + \chi_{zzz}^{(2)} E_z(\omega)^2 + 2\chi_{zxy}^{(2)} E_x(\omega) E_y(\omega) \end{bmatrix} \quad (4.14)$$

$$= \varepsilon_0 \begin{bmatrix} -2\chi_{xyz}^{(2)} \sin \theta E_s(\omega) E_p(\omega) + 2\chi_{xxz}^{(2)} \sin \theta \cos \theta E_p(\omega)^2 \\ -2\chi_{yzy}^{(2)} \sin \theta E_s(\omega) E_p(\omega) + 2\chi_{yzx}^{(2)} \sin \theta \cos \theta E_p(\omega)^2 \\ \chi_{zxx}^{(2)} \cos^2 \theta E_p(\omega)^2 + \chi_{zzz}^{(2)} \sin^2 \theta E_p(\omega)^2 + \chi_{zyy}^{(2)} E_s(\omega)^2 - 2\chi_{zxy}^{(2)} \cos \theta E_p(\omega) E_s(\omega) \end{bmatrix} \quad (4.15)$$

where $\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)}$, inside the plane of sample surface.

To give a detailed definition of these non-vanishing elements of $\chi^{(2)}$ in terms of hyperpolarizability tensor β , there are expressions based on molecular coordinates, where the arrangement of molecules at the interface is characterized by an average tilt angle δ of the molecular axis along $\vec{z}$.⁵

$$\begin{pmatrix} \chi_{ZZZ}^{(2)} \\ \chi_{ZXX}^{(2)} \\ \chi_{XZX}^{(2)} \\ \chi_{XXZ}^{(2)} \end{pmatrix} = \frac{N_\sigma}{\epsilon_0} \begin{bmatrix} a & 2b & 2b & 2b \\ 2b & c & -b & -b \\ 2b & -b & c & -b \\ 2b & -b & -b & c \end{bmatrix} \begin{pmatrix} \beta_{zzz} \\ \beta_{zxx} + \beta_{zyy} \\ \beta_{xzx} + \beta_{yzy} \\ \beta_{xxz} + \beta_{yyz} \end{pmatrix} \quad (4.16)$$

where N_σ is the number of molecules per unit area, and $a = \cos^3 \delta$,

$b = \frac{1}{4}(\cos \delta - \cos^3 \delta)$, $c = \frac{1}{4}(\cos \delta + \cos^3 \delta)$. When Kleinman symmetry holds, there is

$$\chi_{XXZ}^{(2)} = \chi_{ZZX}^{(2)} \text{ and } \chi_{YZY}^{(2)} = \chi_{ZYY}^{(2)}.$$

Also, there is

$$\begin{pmatrix} \chi_{XYZ}^{(2)} \\ \chi_{YZX}^{(2)} \\ \chi_{ZXY}^{(2)} \end{pmatrix} = \frac{N_\sigma}{\epsilon_0} \begin{bmatrix} d & e & e \\ e & d & e \\ e & e & d \end{bmatrix} \begin{pmatrix} \beta_{xyz} - \beta_{yxz} \\ \beta_{yzx} - \beta_{xzy} \\ \beta_{zxy} - \beta_{zyx} \end{pmatrix} \quad (4.17)$$

where $d = \frac{1}{2}\cos^2 \delta$, $e = \frac{1}{4}(1 - \cos^2 \delta)$ and there is $\chi_{XYZ}^{(2)} = -\chi_{YZX}^{(2)}$.⁶

Therefore, equation (4.15) can be simplified as

$$\begin{bmatrix} P_X(2\omega) \\ P_Y(2\omega) \\ P_Z(2\omega) \end{bmatrix} = \epsilon_0 \begin{bmatrix} -2\chi_{XYZ}^{(2)} \sin \theta E_s(\omega) E_p(\omega) + 2\chi_{ZXX}^{(2)} \sin \theta \cos \theta E_p(\omega)^2 \\ -2\chi_{ZXX}^{(2)} \sin \theta E_s(\omega) E_p(\omega) - 2\chi_{XYZ}^{(2)} \sin \theta \cos \theta E_p(\omega)^2 \\ \chi_{ZXX}^{(2)} \cos^2 \theta E_p(\omega)^2 + \chi_{ZXX}^{(2)} E_s(\omega)^2 + \chi_{ZZZ}^{(2)} \sin^2 \theta E_p(\omega)^2 - 2\chi_{ZXY}^{(2)} \cos \theta E_p(\omega) E_s(\omega) \end{bmatrix} \quad (4.18)$$

where there are only four susceptibility elements to be considered.

As discussed in Chapter 3, SHG-ORD and SHG-CD⁴ both prove that chirality is induced in chiral-modified Ag NPs. Here we will give a theoretical interpretation to these results, aiming to separate the second-order contributions from chiral and achiral susceptibilities.

4.2.1 SHG-ORD

In our experiments, assuming $\frac{n_{glass}^{2\omega}}{n_{glass}^{\omega}} \approx 1$, then we have the approximation

$$\sin \theta'' \approx \sin \theta \Rightarrow \theta'' \approx \theta.$$

For an exactly p-polarized fundamental light, $E_s(\omega) = 0$. Equation (4.15) becomes

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = \varepsilon_0 E_p(\omega)^2 \begin{bmatrix} 2\chi_{ZXX}^{(2)} \sin \theta \cos \theta \\ -2\chi_{XYZ}^{(2)} \sin \theta \cos \theta \\ \chi_{ZXX}^{(2)} \cos^2 \theta + \chi_{ZZZ}^{(2)} \sin^2 \theta \end{bmatrix} \quad (4.19)$$

where there are only three susceptibility elements to be discussed.

In SHG-ORD, second harmonic intensity analyzed at linearly +45°-polarization,

where $I_{+45^\circ}(2\omega) \propto |\mathbf{P}_{+45^\circ}(2\omega)|^2 = |\mathbf{P}(2\omega) \cdot \mathbf{l}_{+45^\circ}|^2$, can be expressed as

$$\begin{aligned} I_{+45^\circ}(2\omega) &\approx \varepsilon_0^2 T_p I_p(\omega)^2 \left| \chi_{eff}^{(2)} f(\sin \theta, \cos \theta) \cdot \mathbf{l}_{+45^\circ} \right|^2 \\ &= \varepsilon_0^2 T_p I_p(\omega)^2 \left[\sqrt{2} \chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta + \sqrt{2} \chi_{XYZ}^{(2)} \sin \theta \cos \theta + \sqrt{2} \chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta + \sqrt{2} \chi_{ZZZ}^{(2)} \sin^3 \theta \right]^2 \\ &= 2 \varepsilon_0^2 T_p I_p(\omega)^2 \left[\chi_{XYZ}^{(2)} \sin \theta \cos \theta + 2 \chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta + \chi_{ZZZ}^{(2)} \sin^3 \theta \right]^2 \end{aligned} \quad (4.20)$$

Similarly, for second harmonic intensity analyzed at linearly -45 °-polarization,

where $I_{-45^\circ}(2\omega) \propto |\mathbf{P}_{-45^\circ}(2\omega)|^2 = |\mathbf{P}(2\omega) \cdot \mathbf{l}_{-45^\circ}|^2$, there is

$$\begin{aligned}
I_{-45^\circ}(2\omega) &\approx \varepsilon_0^2 T_p I_p(\omega)^2 \left| \chi_{eff}^{(2)} f(\sin \theta, \cos \theta) \cdot \mathbf{l}_{-45^\circ} \right|^2 \\
&= \varepsilon_0^2 T_p I_p(\omega)^2 \left[\sqrt{2} \chi_{XX}^{(2)} \sin \theta \cos^2 \theta - \sqrt{2} \chi_{XY}^{(2)} \sin \theta \cos \theta + \sqrt{2} \chi_{ZZ}^{(2)} \sin \theta \cos^2 \theta + \sqrt{2} \chi_{ZZ}^{(2)} \sin^3 \theta \right]^2 \\
&= 2 \varepsilon_0^2 T_p I_p(\omega)^2 \left[-\chi_{XY}^{(2)} \sin \theta \cos \theta + 2 \chi_{XX}^{(2)} \sin \theta \cos^2 \theta + \chi_{ZZ}^{(2)} \sin^3 \theta \right]^2
\end{aligned} \tag{4.21}$$

Therefore, second harmonic intensity difference between +45 ° and -45 ° polarizations (ORD) is written as

$$\begin{aligned}
I_{+45^\circ}(2\omega) - I_{-45^\circ}(2\omega) &= \\
&2 \varepsilon_0^2 T_p I_p(\omega)^2 \left[\chi_{XY}^{(2)} \sin \theta \cos \theta + 2 \chi_{XX}^{(2)} \sin \theta \cos^2 \theta + \chi_{ZZ}^{(2)} \sin^3 \theta \right]^2 \\
&- 2 \varepsilon_0^2 T_p I_p(\omega)^2 \left[-\chi_{XY}^{(2)} \sin \theta \cos \theta + 2 \chi_{XX}^{(2)} \sin \theta \cos^2 \theta + \chi_{ZZ}^{(2)} \sin^3 \theta \right]^2 \\
&= 8 \varepsilon_0^2 T_p I_p(\omega)^2 \left[\chi_{XY}^{(2)} \sin \theta \cos \theta \right] \times \left[2 \chi_{XX}^{(2)} \sin \theta \cos^2 \theta + \chi_{ZZ}^{(2)} \sin^3 \theta \right]
\end{aligned} \tag{4.22}$$

As introduced in Chapter 1, for achiral materials with $C_{\infty v}$ symmetry, there is no

$\chi_{XY}^{(2)}$ element. Substituting $\chi_{XY}^{(2)} = 0$ into equation (4.22), it gives

$$I_{+45^\circ}(2\omega) - I_{-45^\circ}(2\omega) = 0 \tag{4.23}$$

Obviously, equation (4.23) corresponds to the experimental results of SHG-ORD in unmodified Ag NPs.

Therefore, the chiral component $\chi_{chiral}^{(2)}$ only comes from $\chi_{XY}^{(2)}$. As a consequence,

$\chi_{XX}^{(2)}$ and $\chi_{ZZ}^{(2)}$ belong to the achiral component $\chi_{achiral}^{(2)}$.

As is known, a pair of enantiomers possess opposite chirality. For the nonlinear susceptibilities of L-Cysteine and D-Cysteine, it is supposed to have

$$\chi_{chiral}^{(2)}(\text{L-C}) = -\chi_{chiral}^{(2)}(\text{D-C}) \quad (4.24)$$

which indicates an opposite sign with the same value.

Equation (4.22) can be simplified as

$$I_{+45^\circ}(2\omega) - I_{-45^\circ}(2\omega) = 8\varepsilon_0^2 T_p I_p(\omega)^2 f(\sin\theta, \cos\theta) \chi_{chiral}^{(2)} \chi_{achiral}^{(2)} \quad (4.25)$$

According to experimental results of SHG-ORD discussed in Chapter 3, L-C/Ag NPs and D-C/Ag NPs exhibit a reversed value in $I_{+45^\circ}(2\omega) - I_{-45^\circ}(2\omega)$. However, comparing second-order susceptibilities of L-C/Ag NPs with D-C/Ag NPs, there is no difference in $\chi_{achiral}^{(2)}$, which originates from Ag NPs. Therefore, there must be $\chi_{chiral}^{(2)}(\text{L-C/AgNPs}) = -\chi_{chiral}^{(2)}(\text{D-C/AgNPs})$.

4.2.2 SHG-CD

In SHG-CD, the fundamental light is circularly polarized with $E_p = \pm iE_s$, where the upper and lower sign corresponds to right and left circular polarization respectively.⁷

For a right circularly polarized fundamental light, equation (4.18) becomes

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = \varepsilon_0 E_s(\omega)^2 \begin{bmatrix} -2i\chi_{XYZ}^{(2)} \sin\theta - 2\chi_{ZXX}^{(2)} \sin\theta \cos\theta \\ -2i\chi_{ZXX}^{(2)} \sin\theta + 2\chi_{XYZ}^{(2)} \sin\theta \cos\theta \\ -\chi_{ZXX}^{(2)} \cos^2\theta + \chi_{ZXX}^{(2)} - \chi_{ZZZ}^{(2)} \sin^2\theta - 2i\chi_{ZXY}^{(2)} \cos\theta \end{bmatrix} \quad (4.26)$$

According to equation (4.12) and (4.2), second harmonic intensity analyzed at p-polarization, where $I_p(2\omega) \propto |\mathbf{P}_p(2\omega)|^2 = |\mathbf{P}(2\omega) \cdot \mathbf{p}|^2$, can be expressed as

$$\begin{aligned} I_p^{Right}(2\omega) &\approx \varepsilon_0^2 T_s I_s(\omega)^2 \left| \chi_{eff}^{(2)} f(\sin \theta, \cos \theta) \cdot \mathbf{p} \right|^2 \\ &= \varepsilon_0^2 T_s I_s(\omega)^2 \left[-2i\chi_{XYZ}^{(2)} \sin \theta \cos \theta - 3\chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta - \chi_{ZZZ}^{(2)} \sin^3 \theta + \chi_{ZXX}^{(2)} \sin \theta - 2i\chi_{ZXY}^{(2)} \sin \theta \cos \theta \right]^2 \end{aligned} \quad (4.27)$$

Similarly, for a left circularly polarized fundamental light, equation (4.18) becomes

$$\begin{bmatrix} P_X(2\omega) \\ P_Y(2\omega) \\ P_Z(2\omega) \end{bmatrix} = \varepsilon_0 E_s(\omega)^2 \begin{bmatrix} 2i\chi_{XYZ}^{(2)} \sin \theta - 2\chi_{ZXX}^{(2)} \sin \theta \cos \theta \\ 2i\chi_{ZXX}^{(2)} \sin \theta + 2\chi_{XYZ}^{(2)} \sin \theta \cos \theta \\ -\chi_{ZXX}^{(2)} \cos^2 \theta + \chi_{ZXX}^{(2)} - \chi_{ZZZ}^{(2)} \sin^2 \theta + 2i\chi_{ZXY}^{(2)} \cos \theta \end{bmatrix} \quad (4.28)$$

Second harmonic intensity analyzed at p-polarization is then given by

$$\begin{aligned} I_p^{Left}(2\omega) &\approx \varepsilon_0^2 T_s I_s(\omega)^2 \left| \chi_{eff}^{(2)} f(\sin \theta, \cos \theta) \cdot \mathbf{p} \right|^2 \\ &= \varepsilon_0^2 T_s I_s(\omega)^2 \left[2i\chi_{XYZ}^{(2)} \sin \theta \cos \theta - 3\chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta - \chi_{ZZZ}^{(2)} \sin^3 \theta + \chi_{ZXX}^{(2)} \sin \theta + 2i\chi_{ZXY}^{(2)} \sin \theta \cos \theta \right]^2 \end{aligned} \quad (4.29)$$

Second harmonic intensity difference due to opposite circular polarization of the fundamental light can be written as

$$\begin{aligned} I_p^{Right}(2\omega) - I_p^{Left}(2\omega) &= \\ &\varepsilon_0^2 T_s I_s(\omega)^2 \left[-2i\chi_{XYZ}^{(2)} \sin \theta \cos \theta - 3\chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta - \chi_{ZZZ}^{(2)} \sin^3 \theta + \chi_{ZXX}^{(2)} \sin \theta - 2i\chi_{ZXY}^{(2)} \sin \theta \cos \theta \right]^2 \\ &- \\ &\varepsilon_0^2 T_s I_s(\omega)^2 \left[2i\chi_{XYZ}^{(2)} \sin \theta \cos \theta - 3\chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta - \chi_{ZZZ}^{(2)} \sin^3 \theta + \chi_{ZXX}^{(2)} \sin \theta + 2i\chi_{ZXY}^{(2)} \sin \theta \cos \theta \right]^2 \\ &= 8i\varepsilon_0^2 T_s I_s(\omega)^2 \left[3\chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta + \chi_{ZZZ}^{(2)} \sin^3 \theta - \chi_{ZXX}^{(2)} \sin \theta \right] \times \left[\chi_{XYZ}^{(2)} \sin \theta \cos \theta + \chi_{ZXY}^{(2)} \sin \theta \cos \theta \right] \\ &= 4i\varepsilon_0^2 T_s I_s(\omega)^2 \sin 2\theta \left[3\chi_{ZXX}^{(2)} \sin \theta \cos^2 \theta + \chi_{ZZZ}^{(2)} \sin^3 \theta - \chi_{ZXX}^{(2)} \sin \theta \right] \times \left[\chi_{XYZ}^{(2)} + \chi_{ZXY}^{(2)} \right] \end{aligned} \quad (4.30)$$

which behaves as the imaginary part of a complex.

For achiral materials with $C_{\infty v}$ symmetry, there are $\chi_{XYZ}^{(2)} = 0$ and $\chi_{ZXY}^{(2)} = 0$, which gives

$$I_p^{Right}(2\omega) - I_p^{Left}(2\omega) = 0 \quad (4.31)$$

As concluded from SHG-ORD, $\chi_{ZXX}^{(2)}$ and $\chi_{ZZZ}^{(2)}$ belong to the achiral component $\chi_{achiral}^{(2)}$. Hence, according to equation (4.30), chiral component $\chi_{chiral}^{(2)}$ includes $\chi_{XYZ}^{(2)}$ and $\chi_{ZXY}^{(2)}$, which only exist for chiral materials with C_∞ symmetry. Equation (4.30) can also be simplified as

$$I_p^{Right}(2\omega) - I_p^{Left}(2\omega) = 4i\varepsilon_0^2 T_s I_s(\omega)^2 \sin 2\theta f(\sin \theta, \cos \theta) \chi_{chiral}^{(2)} \chi_{achiral}^{(2)} \quad (4.32)$$

According to experimental results of SHG-CD discussed in Chapter 3, chiral-modified Ag NPs present a non-zero value in $I_p^{Right}(2\omega) - I_p^{Left}(2\omega)$. Therefore, there must be $\chi_{XYZ}^{(2)} = \chi_{ZXY}^{(2)}$, which stands for the Kleinman symmetry. Also, L-C/Ag NPs and D-C/Ag NPs exhibit a reversed result in SHG-CD. As there is no difference in $\chi_{achiral}^{(2)}$, obviously, there must be $\chi_{chiral}^{(2)}(\text{L-C/Ag NPs}) = -\chi_{chiral}^{(2)}(\text{D-C/Ag NPs})$, which indicates an opposite sign with the same value in $\chi_{XYZ}^{(2)}$. This conclusion also agrees with the theoretical illustration in SHG-ORD.

4.2.3 Discussion on Ag NPs modified by mixture of L-Cysteine and D-Cysteine

In Chapter 3, SHG-ORD of Ag NPs modified by mixture of L-Cysteine and D-Cysteine were finally discussed, which further proves the existence of opposite chirality between L-C/Ag NPs and D-C/Ag NPs.

According to equation (4.25), the maximum difference of SHG-ORD is given by

$$\begin{aligned}\Delta_{ORD}^{MAX} &= \left(I_{+45^\circ}(2\omega) - I_{-45^\circ}(2\omega) \right)_{\theta=\theta_{MAX}} \\ &= 8\varepsilon_0^2 T_p I_p(\omega)^2 f(\sin \theta_{MAX}, \cos \theta_{MAX}) \chi_{achiral}^{(2)} \chi_{chiral}^{(2)}\end{aligned}\quad (4.33)$$

If there is $\chi_{chiral}^{(2)}(\text{L-C}) = \chi_{XYZ}^{(2)}$ for L-C/Ag NPs, thus, for D-C/Ag NPs, there is $\chi_{chiral}^{(2)}(\text{D-C}) = -\chi_{XYZ}^{(2)}$. In the mixture of L-Cysteine and D-Cysteine, let us assume that the chiral component of the second-order susceptibility is related to the ratio of D-Cysteine or L-Cysteine, which can be simply written as

$$\begin{aligned}\chi_{chiral}^{(2)}(\text{L-C/D-C}) &= R_{L-C} \chi_{chiral}^{(2)}(\text{L-C}) + R_{D-C} \chi_{chiral}^{(2)}(\text{D-C}) \\ &= (1 - R_{D-C}) \chi_{XYZ}^{(2)} - R_{D-C} \chi_{XYZ}^{(2)} \\ &= \chi_{XYZ}^{(2)} - 2R_{D-C} \chi_{XYZ}^{(2)}\end{aligned}\quad (4.34)$$

where R_{L-C} and R_{D-C} represent the ratio of L-Cysteine and D-Cysteine in their mixture.

It is supposed that there is no difference in $\chi_{achiral}^{(2)}$ and θ_{MAX} is approximately the same for each sample, by substituting equation (4.34), equation (4.33) would become

$$\begin{aligned}\Delta_{ORD}^{MAX} &= 8\varepsilon_0^2 T_p I_p(\omega)^2 f(\sin \theta_{MAX}, \cos \theta_{MAX}) \chi_{achiral}^{(2)} [\chi_{XYZ}^{(2)} - 2R_{D-C} \chi_{XYZ}^{(2)}] \\ &= \text{Slope} R_{D-C} + \text{Intercept}\end{aligned}\quad (4.35)$$

Hence, Δ_{ORD}^{MAX} has a linear relation with R_{D-C} , which agrees with the linear fitting result of Figure 3.14 in Chapter 3.

4.3 Calculation of Second-Order Susceptibilities

Based on those theoretical interpretations illustrated in section 4.2, we have

$$\chi_{chiral}^{(2)} = \chi_{XYZ}^{(2)} \text{ and } \chi_{achiral}^{(2)} = \chi_{ZXX}^{(2)}, \chi_{ZZZ}^{(2)} \quad (4.36)$$

So there are only three susceptibility elements to be calculated. Here we will use theoretical fittings of SHG-ORD from L-C/Ag NPs and D-C/Ag NPs, which involves both $\chi_{chiral}^{(2)}$ and $\chi_{achiral}^{(2)}$, on purpose of finding out relative values of second-order susceptibilities. For a simplified calculation, error bars during fitting processes are ignored.

According to equation (4.20), there is

$$\sqrt{I_{+45^\circ}(2\omega)} = \sqrt{2\varepsilon_0^2 T_p I_p(\omega)^2} \left[\frac{1}{2} \chi_{XYZ}^{(2)} \sin 2\theta + \chi_{ZXX}^{(2)} \sin 2\theta \cos \theta + \chi_{ZZZ}^{(2)} \sin^3 \theta \right] \quad (4.37)$$

Thus, equation (4.37) can be directly used to give a theoretical fitting of SHG-ORD analyzed at $+45^\circ$ polarization, with fitting coefficients including $\chi_{XYZ}^{(2)}$, $\chi_{ZXX}^{(2)}$ and $\chi_{ZZZ}^{(2)}$. Figure 4.3 and Figure 4.4 present theoretical fittings of SHG-ORD of L-C/Ag NPs and D-C/Ag NPs respectively.

Figure 4.3 SHG of L-C/Ag NPs. Fundamental: p-polarized. Second harmonic: +45 °polarized.
Solid line: theoretical fitting to equation (4.37), $R^2=0.93$.

Figure 4.4 SHG of D-C/Ag NPs. Fundamental: p-polarized. Second harmonic: +45 °polarized.
Solid line: theoretical fitting to equation (4.37), $R^2=0.97$.

Similarly, for SHG-ORD analyzed at -45 °polarization of second harmonic signals, according to equation (4.21), there is

$$\sqrt{I_{-45^\circ}(2\omega)} = \sqrt{2\varepsilon_0^2 T_p I_p(\omega)^2} \left[-\frac{1}{2} \chi_{XYZ}^{(2)} \sin 2\theta + \chi_{ZXX}^{(2)} \sin 2\theta \cos \theta + \chi_{ZZZ}^{(2)} \sin^3 \theta \right] \quad (4.38)$$

which can be used for the theoretical fitting. Figure 4.5 and Figure 4.6 present theoretical fittings of SHG-CD of L-C/Ag NPs and D-C/Ag NPs respectively.

Figure 4.5 SHG of L-C/Ag NPs. Fundamental: p-polarized. Second harmonic: -45 °polarized.
Solid line: theoretical fitting to equation (4.38), $R^2=0.97$.

Figure 4.6 SHG of D-C/Ag NPs. Fundamental: p-polarized. Second harmonic: -45 °polarized.

Solid line: theoretical fitting to equation (4.38), $R^2=0.96$.

According to fitting coefficients obtained from simulated curves, relative values of $\chi_{chiral}^{(2)}$ and $\chi_{achiral}^{(2)}$ are obtained in Table 4.1 and Table 4.2, where the second-order susceptibilities are presented in an arbitrary unit.

Second Harmonic Polarization		+45 °	Standard Error(+45 °)	-45 °	Standard Error(-45 °)
$\chi_{chiral}^{(2)}$	$\chi_{XYZ}^{(2)}$ (a.u.)	-1.2	0.5	-1.1	0.4
$\chi_{achiral}^{(2)}$	$\chi_{ZXX}^{(2)}$ (a.u.)	1.0	0.3	1.4	0.2
	$\chi_{ZZZ}^{(2)}$ (a.u.)	0.6	0.2	0.7	0.1

Table 4.1 Second-order susceptibilities of L-C/Ag NPs.

Second Harmonic Polarization		+45 °	Standard Error(+45 °)	-45 °	Standard Error(-45 °)
$\chi_{chiral}^{(2)}$	$\chi_{XYZ}^{(2)}$ (a.u.)	1.9	0.2	1.7	0.3
$\chi_{achiral}^{(2)}$	$\chi_{ZZX}^{(2)}$ (a.u.)	1.0	0.1	0.9	0.1
	$\chi_{ZZZ}^{(2)}$ (a.u.)	0.8	0.1	0.6	0.1

Table 4.2 Second-order susceptibilities of D-C/Ag NPs.

Here, we don't put the exact value of surface susceptibility $\chi^{(2)}$. This calculation requires knowledge of thickness and surface properties which we are not sure.

As a conclusion, based on the results of SHG-ORD in chiral-modified Ag NPs, it is possible to separate and calculate chiral and achiral susceptibilities, which roughly agree with our theoretical interpretations.

Because the theoretical calculation of SHG-CD can be more complex as it includes imaginary parts, SHG-ORD is a better method for a quantitative analysis of chirality. Theoretical fittings of other SHG results presented in Chapter 3 can be found in Appendix C, which are roughly fitted based on equation (4.12).

4.4 Summary

In Chapter 4, basic theory of SHG dependent on incidence is introduced, especially applied into chiral-modified Ag NPs with C_∞ symmetry as introduced in Chapter 1. To find out chiral and achiral contributions to second-order susceptibilities, simplified

interpretations of SHG-ORD and SHG-CD are given based on several assumptions, which finally prove that there are $\chi_{chiral}^{(2)} = \chi_{XYZ}^{(2)}$ and $\chi_{achiral}^{(2)} = \chi_{ZXX}^{(2)}, \chi_{ZZZ}^{(2)}$. Through theoretical fittings of results presented in Chapter 3, those three susceptibility elements are calculated and given with relative values, which roughly correspond to the previous theory. Although all the simulations are founded on ideal conditions and simplified a lot, which ignore absorption, SP effects and etc., this is a proper theoretical model, which interprets the observation of chirality in SHG of chiral-modified Ag NPs.

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Chapter 5

Conclusion and Future Work

5.1 Conclusion

We have fabricated chiral-modified Ag NPs attached with cysteine and investigated SHG properties of modified and unmodified Ag NPs.

For unmodified Ag NPs, deposition thickness plays an important role in the observation of SHG, where wavelength of SPR varies with deposition thickness and SPR may help the detection of an enhanced second harmonic intensity. Transmitted SHG of Ag NPs, which is dependent on incidence, were successfully detected in our experimental set-up.

For modified Ag NPs, chiral molecules of either L-Cysteine or D-Cysteine, as a pair of enantiomers, were used to modify Ag NPs respectively. Nonlinear optical rotation, also termed as SHG-ORD, which is described by the difference of $\pm 45^\circ$ output polarization of SHG, is observed reversely between L-C/Ag NPs and D-C/Ag NPs. However, no optical rotation exists for Ag NPs alone. SHG-ORD proves that opposite chirality is induced in L-C/Ag NPs and D-C/Ag NPs through the chiral-modification process, where additional second-order susceptibility elements are involved. Similarly, another experiment of chiral proofs in modified Ag NPs, termed as SHG-CD, which is described by the second harmonic difference of input right and left circular polarization, is also observed reversely between L-C/Ag NPs and D-C/Ag NPs. SHG-CD again proves the existence of chirality in chiral-modified Ag NPs. To find out the influence of chirality,

SHG-ORD of Ag NPs modified with a mixture of L-Cysteine and D-Cysteine, where the ratio of D-Cysteine is linearly changed, was conducted at the optimum incident angle, which is referred to a maximum optical rotator difference. As we noticed that the maximum difference of SHG-ORD also has a linear relation with the ratio of D-Cysteine, thus it can be further verified that there is an opposite chirality between L-C/Ag NPs and D-C/Ag NPs, which is induced by chiral molecules.

As introduced in Chapter 1, chiral materials possess additional second-order susceptibilities compared with achiral materials, due to the difference of symmetries. Therefore, SHG-ORD and SHG-CD have been used to investigate chirality. Hence, for chiral-modified Ag NPs, it would be possible to assess the second-order susceptibilities separately into chiral and achiral parts. Derived from the elementary theory of SHG, we have illustrated chiral and achiral susceptibility components through theoretical interpretations of SHG-ORD and SHG-CD in chiral-modified Ag NPs, and presented relative values of those susceptibilities through theoretical fittings.

As a conclusion, SHG is an efficient probing method for distinguishing L-Cysteine from D-Cysteine in chiral-modified Ag NPs, which is an alternative diagnostic of chirality in molecules.

5.2 Future Work

As calculated in Chapter 3, the efficiency of SHG in our experiments is rather weak, which may influence the stability of results a lot. To increase SHG efficiency under the same experimental set-up, it may be reasonable to increase the noncentrosymmetry first,

through fabricating arrayed Ag NPs¹ compared with a random distribution of Ag NPs obtained by vacuum thermal evaporation. Also, metallic nanotubes with an adjusting length and diameter, is also a promising choice for enhancing second harmonic intensity excited by an IR wavelength.²

For chiral-modified Ag NPs on glass substrate, the amount of chiral molecules attached to silver through the self-assembly process is quite limited. If multilayers of chiral molecules could be coated on top of Ag NPs, second harmonic effect due to nonlinear susceptibilities from the chiral component would be theoretically enhanced, where SHG-ORD and SHG-CD of modified Ag NPs may exhibit a stronger difference.

To have a deeper understanding of the mechanism of SHG of chiral-modified Ag NPs and the induced chirality, it is interesting to find out whether the difference in SHG-ORD or SHG-CD is from cysteine itself or the assembled structure of cysteine and silver. The idea of adding a proper spacer polymer³ with a controlled thickness, which could be sandwiched between the layer of cysteine and Ag NPs, may be a solution to help modeling these results of SHG.

As suggested above, taking advantage of the sensitivity and precision of SHG, it would be exciting to develop chiral-modified Ag NPs into an optical sensor in the diagnosis of chirality.

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Appendix A

Circular dichroism spectra of L-Cysteine and D-Cysteine

Source of figures: J. Nan and X.P. Yan, A circular dichroism probe for L-Cysteine based on self-assembly of chiral complex nanoparticles, *Chem. Eur. J.* 16, 423-427 (2010).

Figure A.1 Circular dichroism spectra of L-Cysteine (-, 50 μ M), Ag (-, 50 μ M), and a mixture (· · ·) L-Cysteine (50 μ M) and Ag (50 μ M). The measurement was taken immediately after mixing.

Figure A.2 Circular dichroism spectra of the mixture of (a) L-Cysteine (10 μ M) and Ag (11 μ M), (b) D-Cysteine (10 μ M) and Ag (11 μ M) measured after ultrasonication (120W) in a water bath at 37°C for 30 min.

Appendix B

Figure B.1 SHG of Ag NPs excited by p-polarized fundamental light, where second harmonic light is analyzed at p/s/ $\pm 45^\circ$ output polarization.

Figure B.2 SHG of L-C/Ag NPs excited by p-polarized fundamental light, where second harmonic light is analyzed at p/s/ $\pm 45^\circ$ output polarization.

Figure B.3 SHG of D-C/Ag NPs excited by p-polarized fundamental light, where second harmonic light is analyzed at p/s/ $\pm 45^\circ$ output polarization.

Appendix C

The following theoretical fittings are all done by Origin Lab.

Figure C.1 SHG of Ag NPs, excited by p-polarized fundamental light, where second harmonic light is analyzed at p- and s- output polarization. Fittings are based on equation (4.12).

Figure C.2 SHG of L-C/Ag NPs, excited by p-polarized fundamental light, where second harmonic light is analyzed at p- and s- output polarization. Fittings are based on equation (4.12).

Figure C.3 SHG of D-C/Ag NPs, excited by p-polarized fundamental light, where second harmonic light is analyzed at p- and s- output polarization. Fittings are based on equation (4.12).

Figure C.4 SHG-ORD of Ag NPs. Fittings are based on equation (4.20) and (4.21).

Figure C.5 SHG-CD of L-C/Ag NPs. Fittings are based on equation (4.27) and (4.29).

Figure C.6 SHG-CD of D-C/Ag NPs. Fittings are based on equation (4.27) and (4.29).