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Interaction of Molecules and Helical Nanoparticles Characterized by Electronic Circular Dichroism

YANG Lin

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Principal Supervisor: Dr. HUANG Jeffrey

Hong Kong Baptist University
August 2018
DECLARATION

I hereby declare that this thesis represents my own work which has been done after registration for the degree of PhD at Hong Kong Baptist University, and has not been previously included in a thesis or dissertation submitted to this or any other institution for a degree, diploma or other qualifications.

I have read the University’s current research ethics guidelines and accept responsibility for the conduct of the procedures in accordance with the University’s Committee on the Use of Human & Animal Subjects in Teaching and Research (HASC). I have attempted to identify all the risks related to this research that may arise in conducting this research, obtained the relevant ethical and/or safety approval (where applicable), and acknowledged my obligations and the rights of the participants.

Signature: __________________

Date: August 2018
Abstract

It is of fundamental significance to differentiate an enantiomer from its mirror image (i.e., enantiodifferentiation), through monitoring optical activity (OA) of enantiomers that is typically characterized by electronic circular dichroism (ECD or CD) in the UV-visible region. However, sub-wavelength molecular dimensions substantially prevent enantiomers from effectively perceiving the different circular polarization states, leading to low enantiomeric OA and weak enantiodifferentiation. Some approaches have been developed to amplify the enantiomeric OA; alternatively, on the basis of the emerging chiral metamaterials of metallic helical nanoparticles (HNPs) I devise two methods to enhance the enantiodifferentiation.

First, I employ glancing angle deposition (GLAD) to deposit Ag HNPs with a helical pitch ($P$) larger than wire diameter ($d$) of the helical, i.e., Ag nanohelices (AgNHs). AgNHs exhibit strong plasmonic CD composed of a broadband longitudinal mode (i.e., L-mode) in the visible region, a transverse mode (i.e., T-mode) at a wavelength of ~370 nm, and a dielectric mode in the deep UV region (at a wavelength shorter than 320 nm). Adsorption of alkyl ligands on the AgNHs markedly weakens the two plasmonic CD modes, and the T-mode is weakened more seriously than the L-mode. The deterioration of the plasmonic CD is exacerbated with increasing the bonding energy of the Ag-alkyl ligand contacts, attributed to the increase of the dielectric constant of the medium of the AgNHs ($\varepsilon_r$) and the electron withdrawal from the AgNHs towards the alkyl ligands. Derived from the ligand-induced weakening of the plasmonic CD, enantiodifferentiation of L-Glutathione (L-GSH) from D-GSH is dramatically enhanced. The chiroptical weakening sensitively varies with the absolute configuration of GSH, resulting in an enantiodifferentiation anisotropic $g$ factor of ~0.5 that is independent on the AgNH helicity. The AgNH-induced anisotropy $g$ factor is superior to those obtained by other methods, by 2 – 4 orders of magnitude. It is the largest achieved up-to-date, as high as one-fourth of the theoretical maximum.

Second, I operate GLAD with fast substrate rotation to reduce $P$ less than $d$, to generate AgHNPs that exhibit negligible dielectric CD in the deep UV region, offering a helical substrate to directly amplify the OA of enantiomers grafted on the AgHNPs. The anchoring of enantiomers on AgHNPs with the sub-5 nm $P$ leads to the enantioselective amplification of the enantiomeric OA in roughly
ten folds; the LH- and RH-AgHNPs give rise to amplify the OA of (S)- and (R)-enantiomers, respectively. It is ascribed to the change of the dihedral angle of an enantiomer adsorbed on AgHNPs. Such the enantioselective amplification tends not to occur as long as $P > 5$ nm.

Moreover, given the enantiodifferentiation of biomolecules that are typically dissolved in an aqueous solution, the effect of water on the plasmonic CD of AgHNPs is investigated and compared with that of AgNHs. Hydrophobic AgNHs with high structural porosity give rise to the irreversible water effect on the plasmonic CD; and hydrophilic AgHNPs with low structural porosity lead to the reversible water effect.

At the end, I devise a new methodology to generate plasmonic CD through chirality transfer from chiral host to achiral guest, owing to the helicity duplication of the achiral guest from the chiral host. It leads to inducing chiroptical activity of the achiral guest made of some plasmonic materials that aren’t facilely sculptured in the helical. The new methodology effectively broadens the range of materials made from the chiral nanostructures, which is on demand to develop diverse chirality-related bioapplications.
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First of all, I would like to take this opportunity to extend to my sincere gratitude to my supervisor, Dr. Zhifeng Huang, for his valuable, devoted and patient guidance in my doctoral study. His conscientious attitude, enthusiasm and interests in scientific research always motivate me to become a good researcher. Without his invaluable guidance, my research works could not be completed. It is my great honor to be his student studying and working in the group. I really appreciate that he provides such a unique environment and supportive group, from which the experience will prompt me to pursue a higher level in the academic research.

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List of Abbreviations

AgHNP Silver nanoparticle with hidden helicity
AgNH Silver nanohelix
AgNP Silver nanoparticle
AgNR Silver nanorod
AuHNP Gold nanoparticle with hidden helicity
ATR-FTIR Attenuated total reflection Fourier-transform infrared spectroscopy
CB Circular birefringence
CD Circular dichroism
CPL Circularly polarized light
CuHNP Copper nanoparticle with hidden helicity
DLW Direct laser writing
E-beam Electron beam
ECD Electronic circular dichroism
EF Enhancement factor
FIBID Focused ion beam induced deposition
EM field Electromagnetic field
FMN Flavin mononucleotide
Enantiomer 1 1,1’-Binaphthyl benzo-27-crown-8 benzyl (1, 2-dithiolan-3-yl) pentanoate
Enantiomer 2 1,1’-Binaphthyl-2,2’-dithiol
ERSPS 5-enolpyruvylshikimate 3-phosphate synthase
GLAD Glancing angle deposition
GSH Glutathione
ITO Indium tin oxide
LCP Left-handed circularly polarized light
LH Left-handed
L-mode Longitudinal mode
LP Linear polarized light
LSPR Localized surface plasmon resonance
OA Optical activity
ORD Optical rotatory dispersion
PhNP Plasmonic helical nanoparticle
PMMA Methyl methacrylate
QCM Quartz crystal microbalance
RCP Right-handed circularly polarized light
$R_d$ Deposition rate
RH Right-handed
ROA Raman optical activity
SEM Scanning electron microscopy
SEROA Surface enhanced Raman optical activity
SK Shikimate kinase
STED Stimulated-emission depletion
TEM Transmission electron microscopy
TES Template-assisted electrosynthesis
TiO$_2$HNPs Titanium dioxide nanoparticle with hidden helicity
T-mode Transverse mode
VCD Vibrational circular dichroism
XPS X-ray photoelectron spectroscopy
3D Three-dimensional
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1 Introduction

Silver helical structures with intrinsic geometrical chirality exhibit a strong optical response in the ultraviolet (UV) and visible regions. We study the interaction of alkyl ligands and Ag nanohelices (AgNHs) by quantitatively evaluating changes in the circular dichroism (CD) of AgNH arrays induced by grafting alkyl ligands onto AgNHs. CD deterioration is exacerbated when the bonding energy of the Ag-G contacts increases, which is attributed to the increase in $\varepsilon_r$ and electron withdrawal from the AgNHs toward C8-G. Based on our understanding of the interaction, we used an indirect method to differentiate the enantiomeric molecules. L- and D-GSH are chemically grafted onto AgNHs, which leads to weakened chiroptical activity in an AgNH array in the visible region. This weakening sensitively varies with the absolute GSH configuration, which results in differentiation between L- and D-GSH (see Chapter 3).

I discovered a new, enantioselective method of directly amplifying enantiomeric optical activity, which involved covalently grafting enantiomers onto AgHNPs. Enantiomers were grafted onto AgHNPs with sub-5-nm helical pitches, leading to a roughly one order of magnitude amplification of optical activity (OA). The LH- and RH-AgHNPs give rise to amplify the OA of (S)- and (R)-enantiomers, respectively. The adsorption configurations of enantiomers were simulated to reveal that the OA enhancement may be ascribed to the change of the dihedral angle of an enantiomer adsorbed on AgHNPs. Such the enantioselective amplification tends not to occur as long as $P > 5$ nm. (see Chapter 4).

Chirality-related bioapplications are typically operated in water environments, so I then studied the water effect of hidden helical structures. The water effect on the optical activity of AgHNPs caused the plasmonic mode to redshift by $\approx 40$ nm and amplify the CD by $\approx 140\%$. It was markedly reversible in multiple alternating wetting/drying processes. This was ascribed to the surface hydrophilicity and low array porosity. However, the chiroptical activity of AgNHs with $P > d$ tended to be quenched by multiple alternating wetting/drying processes, illustrating the irreversible chiroptical water effect. The reversible water effect was ascribed to the surface hydrophilicity of AgHNPs, and hydrophobic AgNHs accounted for the irreversible water effect (see Chapter 5).
I also demonstrated a new method of chirality transfer from chiral host to achiral guest, leading to induced chiroptical activity in the achiral guest made of plasmonic materials not easily sculptured into helical structures to exhibit the chiroptical activity. This method opens a gateway to developing chiroptical spectroscopies for sensitively detecting absolute configuration (see Chapter 6).

Figure 1.1 The outline of the dissertation. Details are shown in the following chapters.
1.1 Chirality and Enantiodifferentiation

1.1.1 Chirality

Chirality is a geometric property of an object, which denotes that the object cannot be superimposed onto its mirror image. Such a molecular stereoisomer is called an enantiomer. Enantiomers are ubiquitous not only in nature, but also in artwork and daily life. Nature generally adopts helical structures to express chirality, from the mega (e.g., the galaxy) to the macro (e.g., snail shells and honeysuckles winding around their support), micro (e.g., bacterial colonies), supramolecular (e.g., DNA and peptides), molecular (e.g., enantiomers) and atomic scales.

1.1.2 Homochirality

Chirality is substantially relevant to the origin of life and biological functions. Most biological molecules, including sugars, proteins and nucleic acids, exhibit optical activity. All of the 21 amino acids are L-stereoisomers, while sugars are D-stereoisomers. The phenomenon of homochirality is common in biological systems, and leads to chirality-dependent interactions. However, its origin is not clearly understood. Over 90% of the drugs in the global market are chiral. One enantiomer has positive effects, while its counterpart probably has negative side-effects or even fatal effects. Forty or fifty years ago, thalidomide (thalomid) was used to treat morning sickness and insomnia. However, thalidomide usually exists in the form of a racemic mixture consisting of conformations R and S, in which the (R)-thalidomide responds to the symptoms, while the (S)-thalidomide has the serious side effect of causing birth defects. Therefore, the detection technology used to differentiate enantiomers is very important. The structure of thalidomide is shown in Figure 1.2.

Figure 1.2 Thalidomide: S (-) (green) and R (+) (pink) configuration
1.1.3 Enantiodifferentiation

Over 90% of chiral drugs are racemic mixtures composed of equal amounts of two stereoisomeric enantiomers. However, it is essential to produce single-enantiomer drugs. Synthesizing chiral drugs is usually performed in achiral environments, leading to the production of racemic mixture compounds. Therefore, it is necessary to separate one stereoisomer from the other (i.e., enantioseparation). It is also necessary to differentiate one absolute configuration of an enantiomer from the other (i.e., enantiodifferentiation). Several chiroptical spectroscopies have been used to characterize the optical activity of enantiomers that denotes differential responses to left- and right-handed circular polarized light (CPL).

1.2 Optical Activity

The optical activity of an object denotes the differential interaction of left- and right-handed CPL (i.e., LCP and RCP). It is characterized by electronic circular dichroism (ECD or CD, used to monitor the differential absorption of UV-visible near-infrared CPL) and optical rotatory dispersion (ORD, used to monitor the differential real part of the refractive index of an object). Both CD and ORD are powerful tools used in the chiral field for studying enantiomers, and especially for analyzing higher-order protein structures.

Figure 1.3 (a) Linearly polarized light (blue line) could be regarded as a combination of RCP (red line) and LCP (green line). (b) ORD (CB): the refractive index of the samples for LCP and RCP are different; the plane-polarized light will be rotated through an angle Φ. (c) CD: the different absorption of LCP and RCP lead to ellipticity with an angle θ.[4]
Raman optical activity (ROA, used to monitor the differential intensity of the Raman scattered LCP and RCP of an object) is a vibrational spectroscopic technique. Vibrational circular dichroism (VCD, used to monitor the differential absorption of infrared CPL for exciting molecular vibrations) spectroscopy is applied to provide structural information on chiral molecules in the infra-red range in which molecular bond vibrations exist.

![Figure 1.4 The mechanism and detection regions of CD, ORD, ROA and VCD.](image)

In general, the chiral response of natural chiral media is quite weak, because the size of the CPL wavelength and the chiral molecular dimension are mismatched. Furthermore, CD spectroscopy provides quick and simple insights into complicated molecular structures, especially high-order protein structures. Thus, CD spectroscopy was selected as the research method for detecting the chiral responses of molecules and plasmonic structures.

### 1.2.1 CD spectroscopy

CD spectroscopy has been widely used to detect differences in absorbance between LCP and RCP as a function of wavelength. This phenomenon can be observed via CPL through a chiral medium. CD is defined as

\[
CD = \Delta A = A_{LCP} - A_{RCP} \quad (1.1)
\]

where \(A\) denotes absorption, which obeys Beer’s law, as

\[
\Delta A = \Delta \varepsilon Cl = (\varepsilon_{LCP} - \varepsilon_{RCP}) \ Cl \quad (1.2)
\]
where $\varepsilon_{LCP}$ and $\varepsilon_{RCP}$ stand for the molar extinction coefficients of LCP and RCP, respectively, $C$ stands for the molar concentration and $l$ represents the path length. Thus, the difference between the extinction coefficients for the LCP and the RCP equals the difference in absorbance divided by the product of $l$ and $C$ under a specific wavelength:

$$\Delta \varepsilon = \varepsilon_{LCP} - \varepsilon_{RCP} = \Delta A / Cl$$ (1.3)

where $\Delta \varepsilon$ is the molar CD.

Historically, ellipticity is a unit of CD and is defined as the tangent of the ratio of the small ellipse axis to the large ellipse axis. It is still used today, as defined below:

$$\tan \theta = \frac{E_R - E_L}{E_R + E_L}$$ (1.4)

where $E$ stands for the magnitudes of the electric field vectors, and the subscripts “R” and “L” stand for RCP and LCP, respectively.

Figure 1.5 Elliptically polarized light (violet) is caused by RCP (blue) and LCP (red) e-fields with different output magnitudes.

Normally, the CD effect is small, especially for chiral molecules. $\varepsilon$ is relative to the molecular cross section. Then, if the value of $\tan \theta$ is small enough, we can convert $\theta$ to radians. Mathematically, it is defined as
\[ \theta (\text{radians}) \approx \tan \theta = \frac{E_R - E_L}{E_R + E_L} = \sqrt{I_R} - \sqrt{I_L} \] (1.5)

According to Beer’s law,

\[ I = I_0 e^{-A \ln 10} \] (1.6)

Then, with the combination of Eq. (1.5) and Eq. (1.6),

\[ \theta (\text{radians}) = \frac{\left( e^{-\frac{A_R \ln 10}{2}} - e^{-\frac{A_L \ln 10}{2}} \right)}{\left( e^{-\frac{A_R \ln 10}{2}} + e^{-\frac{A_L \ln 10}{2}} \right)} = \frac{\frac{\Delta A}{2} \ln 10 - 1}{\frac{\Delta A}{2} \ln 10 + 1} \] (1.7)

Because \( \Delta A \) is close to 0, after the exponentials are expended and the high-order terms are neglected, Eq. (1.7) can be defined as

\[ \theta (\text{deg}) = \Delta A \left( \frac{\ln 10}{4} \right) \left( \frac{180}{\pi} \right) \] (1.8)

Then, with the combination of Eq. (1.2) and Eq. (1.8),

\[ \theta (\text{mdeg}) = 32982 \Delta \epsilon \text{Cl} \] (1.9)

CD spectra are usually expressed in ellipticity and the unit is usually millidegrees. This is also called standard ellipticity.

CD has been widely applied to characterize optical activity for enantiodifferentiation. It is also used for studying the stereoisomERIC conformation of higher-order proteins and DNA, and conformational changes in chiral molecules due to physical and chemical stimuli. It is well used for estimating \( \alpha \)-helix and \( \beta \)-sheet content and exploring dynamic changes in protein secondary structures (e.g., Figure 1.6).
However, enantiomers typically have sub-wavelength dimensions with respect to UV-visible irradiation, so it is very difficult to perceive their different circular polarizations. The differential absorption is typically $10^{-5}$ of absorption,[5] resulting in weak enantiomeric optical activity and low-sensitivity enantiodifferentiation, especially at low molecular concentrations (e.g., Figure 1.7).

Figure 1.6 Conformation of a peptide with (a) α-helix and (c) β-sheet. (b) CD spectra for these different conformations.

Figure 1.7 Symmetry of the CD spectrum signals of (S)-thalidomide (dashed line) and (R)-thalidomide (solid line) with respect to the x-axis.
The intensity of CD is affected by molecular concentration, because absorption is proportional to concentration. Dissymmetry g-factor is normalized CD that is independent of the concentration and path length of the samples.

### 1.2.2 Dissymmetry g-factor

The g-factor is normalized as the chiral effect and is defined as

\[
g = 2 \frac{\Delta A}{A} = 2 \frac{A_{LCP} - A_{RCP}}{A} \quad (1.10)
\]

where \( A \) stands for the total absorbance of non-polarized light at a specific wavelength.

As the distance between the sample and light source is in the range of the macroscopic scale, CD and g-factor spectra are classified as a far-field effect.

### 1.3 Amplification of Enantiomers’ Optical Activity

One way to achieve enantiodifferentiation is to amplify the optical activity of enantiomers, which is a direct method. Various approaches have been developed to amplifying the optical activity of enantiomers. First, chiroptical spectroscopies have been modified to increase the signal-to-noise ratio of molecular optical activity.[6] Second, molecular excited states can be electrochemically[5] or electronically[7] modified to amplify enantiomeric OA.[8] Third, chirality amplification can be obtained by molecular self-assembly via non-covalent interactions. When chiral analytes are linked to a chromophore, chiral supramolecular assembly causes an efficient chirality transfer from the chiral analytes to the chromophore, leading to the aggregation-induced amplification of the chromophore’s optical activity due to exciton coupling CD.[9, 10] Fourth, high optical chirality of incident CPL, which denotes the chirality density of an electromagnetic field and describes the degree of chiral asymmetry in the excitation rate of enantiomers,[11] is favored for OA amplification. Enhanced optical chirality can be achieved by generating superchiral nodes in the reflection-induced standing wave to achieve 11-fold enhancement,[12] coupling diagonal slits with a mirror to produce homochiral CPL,[13] and using chiral metamaterials (such as plasmonic
1.3.1 Enhancing enantioselectivity by improving the signal-to-noise ratio of chiroptical spectroscopies

Chiroptical spectroscopies are modified to increase the signal-to-noise (S/N) ratio of molecular optical activity,\textsuperscript{[6]} including the ellipsometric self-interference approach\textsuperscript{[16]} and the wave external-interference method.\textsuperscript{[17]}

Chiroptical spectroscopy is a powerful tool for characterizing chiral molecular information by simply detecting the differential chiral responses induced by LCP and RCP. Normally, chiral molecular optical activity is as weak as several millidegrees, which makes it difficult to accurately measure chiroptical signals. Most of chiroptical spectroscopy detection sensitivity is limited by noise occurring during the measurement, which significantly deteriorates the sensitivity of the whole measurement process. Chiroptical spectroscopies are modified to increase the S/N ratio of molecular optical activity, which is a simple way to resolve this problem. Kilger demonstrated the ellipsometric method to amplify the S/N ratio by using elliptically polarized light instead of CPL. This measurement is called “self-heterodyne.” The signal induced by the incident radiation interferes with the incident radiation itself. By controlling the ellipticity of elliptically polarized light, most of the background contribution can be effectively removed without losing the chiral signal. This method can be used for CD and ORD in the UV-visible range. Figures 1.8 (b) and (c) show the CD and ORD spectra of a pair of Ni-(tartrate)\textsubscript{2} and DNA-dye aggregates, respectively, measured using the self-heterodyne method. Both results exhibit greater intensity than the traditional method using CPL as incident light. However, as it is difficult to control incident light in normal operations, this technology is still in the research stage. Therefore, it is still difficult to apply this technology in commercial production.
1.3.2 Amplifying VCD signals by modulating the energies of excited-state manifolds

VCD is a general technology used to characterize the stereochemistry of chiral molecules by using IR irradiation corresponding to the excitation of a vibrational mode in chiral molecules. A one order of magnitude enhancement was observed in a VCD signal when the molecules existed in the anion, rather than the neutral, form. This enhancement was caused by the presence of electrochemical modulation, which “creates” low-lying electronic states. The Sergio R. Domingos and co-authors compared a pair of compounds (R)- and (S)-methyl2-(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl) ((R)-1 and (S)-1) propanoate in the neutral and in the radical anion peak intensities of VCD and IR spectra. The Fourier transform infrared (FTIR) spectra exhibit two existing forms of the molecule: the neutral (blue line) and the radical anion (red line). The VCD spectra of the neutral and anionic (R)-1 and (S)-1 are displayed in the lower panel of Figure 1.10. The authors found that VCD intensity is enhanced in anionic molecules by roughly one order of magnitude, compared to those in neutral form. This is caused by the strong vibration-induced...
mixing of the vibrational excitation state (VE) with the ground state (GS) (Figure 1.10). Therefore, electrochemical VCD is a promising tool for amplifying signals in molecules, even under low concentrations.

Figure 1.9 Vibrational excitation diagram. GS, VE and electron excitation state (EE).

Figure 1.10 (a) IR spectra of neutral (blue line) and radical anion (red line) (R)-1. (b) ORD spectra of (S)-1 and (R)-1 in neutral (blue) and radical anion (red) forms. [5]
1.3.3 Enhancing enantioselectivity by grafting chromophores

Chirality amplification can be obtained by molecular self-assembly via non-covalent interactions (such as electrostatic interaction, hydrogen bonding, host-guest interaction, donor-acceptor interaction, metal-ion coordination, and van der Waals interaction) to generate supramolecular chiral systems, following the “sergeants-and-soldiers principle” and the “majority rules.”[18, 19] When chiral analytes are linked to a chromophore, chiral supramolecular assembly causes an efficient chirality transfer from the chiral analytes to the chromophore, which leads to the aggregation-induced amplification of the chromophore’s optical activity due to exciton coupling CD.[9, 10] Snejana Novkova and co-authors used porphyrins as a chromophore to study the conformation of biopolymers by exciton-coupled CD. Figure 1.11 shows the two terminals of chiral analyte grafted onto several different functional groups (R = 1a, 1b and 1). The authors study the interaction between chiral analyte and chromophores comprised of the change in CD and the absorption of chiral analyte induced by linking the chromophores on chiral analyte. When the two chiral analyte terminals linked with 1a, the CD signal had significant bisignated peaks compared with another compound (R = 1 and 1b). These results demonstrate that a chromophore can extend exciton-coupled CD for conformational analysis of biopolymers. However, the CD signal measured using this method of linking chromophores is actually not the original molecule’s CD signal because the chiral analyte structure has changed.
Figure 1.11 (a) Compound information and CD data. (b) CD and (c) absorption spectra of molecule grafting for each compound.\textsuperscript{20}
1.3.4 Chiral molecular CD enhanced by on-resonance achiral nanoparticles

The excitation of surface plasmons on a metal surface enhances the surface sensitively of several spectra, such as surface-enhanced fluorescence, surface-enhanced Raman spectroscopy and surface enhanced infrared absorption. It holds promise for significantly increasing the chiral response, even for signal-layer molecules or single molecules. Here, L-GS–bimane bonded to the Ag surface, then CD and absorption were enhanced, as electronic transition of the L-GS–bimane overlapped with the Ag plasmonic resonance, as shown in Figure 1.12. The CD enhancement could be naturally regarded as the plasmon-induced resonant absorption enhancement, especially to the larger particles. The enhancement of CD and absorption usually has spectral overlap with the plasmon resonance. However, most bio-molecules have absorption bands in the UV region, which means nanoparticles with shorter wavelength plasmon resonances are needed. For this method, significant enhancement of the sensitivity of CD spectroscopy can also be used for enantiodifferentiation.

Figure 1.12 (a) Absorption spectra of Ag-L-GS bimane (red line), AgNPs without bimane (gray line), L-GS bimane (black line) and the sum of the AgNPs and L-GS-bimane (blue line). (b) CD spectra of L-GS-bimane (thick black line), L-GS-bimane*100 (thin black line), Ag-L-GS bimane (red line), small Ag-L-GS bimane (blue line) and large Ag-L-GS bimane (blue line). [21]
1.3.5 Enhanced enantioselectivity in excitation of chiral molecules by superchiral light

Enantiomeric optical activity can be amplified by the excitation of CPL with high optical chirality, which is denoted as the chirality density of an electromagnetic field. Optical chirality describes the degree of chiral asymmetry in the excitation rate of enantiomers.[11] Optical chirality can be defined as

\[ C = \frac{\varepsilon_0}{2} \mathbf{E} \cdot \nabla \times \mathbf{E} + \frac{1}{2\mu_0} \mathbf{B} \cdot \nabla \times \mathbf{B} \]  \hspace{1cm} (1.11)

where \( \mathbf{E} \) and \( \mathbf{B} \) stand for the electric and magnetic fields, respectively, and \( \mu_0 \) and \( \varepsilon_0 \) are the permeability and permittivity.

Enhanced optical chirality can be achieved by generating superchiral nodes in the reflection-induced standing wave to achieve 11-fold enhancement,[12] coupling diagonal slits with a mirror to produce homochiral CPL,[13] and chiral metamaterials (such as plasmonic gammadion nanostructures,[14] chiral oligomers, and two-armed planar and three-dimensional nanohelices) under resonant excitation of plasmonics nanostructure with chiral shape.[15]

For molecules, a twist in the normal circular polarization field is seldom perceptible at the molecular level. While light is passing through the molecule, the CPL twist is slightly perturbated. However, compared to normal circular polarization fields, superchiral fields present a stronger “twist” under the same frequency, especially when close to the Ue node. Therefore, it is reasonable and promising to increase optical enantioselectivity using the superchiral fields.
In 2011, Tang, Yiqiao and co-authors fabricated a “sandwich” composed of an Al mirror coated with a glass coverslip on one side and chiral molecules on the other. The sample was placed in an optical system that could generate superchiral light. Enhanced optical chirality can be achieved by generating superchiral nodes in the reflection-induced standing wave. The enhancement of enantiomers above one order.
Figure 1.14 Average fluorescence intensity distribution of m-enantiomer and p-enantiomer. Dissymmetry factor with standard deviation at node in chiral (red dot) and achiral (orange dot) situations. The blue line represents the asymmetry factor measured in the chiral thin film without superchiral enhancement. The black demonstrates the theoretical calculation of asymmetric factors. Inset: SEM images.[12]

1.3.6 Enhancing optical chirality of CPL by chiral metamaterial

It is well known that geometrically plasmonic structures can enhance the optical chirality of CPL in the near field of a structure. Plasmonic structures hold promise for enhancing the sensitivity of enantiodifferentiation. Therefore, in this section, the chiral near-field response of a variety of different chiral nanostructures irradiated with CPL is discussed. The interaction between 3D chiral nanostructures and incident light with particular chirality is the strongest and may lead to chiral hot spots, where particularly high optical chirality occurs. In the past few decades, more and more researchers have become interested in the field of plasmonics because chiral nanostructures can significantly enhance the intrinsic optical chirality of CPL in the near field of
chiral nanostructures. For a wide variety of chiral nanostructures, the distribution of enhanced optical chirality irradiated with circular polarized light has been studied. From the results of these simulations, they found that chiral structures can not only enhance electromagnetic field density, but also strongly enhance the optical chirality of CPL in the near fields of nanostructures, whether planar or 3D chiral nanostructures.

A gammadion is a 2D structure that shows a similar chiral response under irradiation with LCP and RCP. The maximum enhancement coefficient is up to 20. A gammadion simultaneously exhibits positive and negative values of optical chirality on its two different sides, no matter whether the light is on the left or right, which means the total enhancement is close to “0.”

Figure 1.15 Optical chirality of CPL enhanced by gold gammadions irradiated with (a) LCP and (b) RCP at a wavelength of 2.01 um. A gammadion’s structure exhibits similar enhanced optical chirality distribution for both types of CPL; only the values differ.[22]
In general, the most common 3D structure is a helical structure, in which the distribution of enhanced optical chirality is quite complicated. In Figure 1.16 (a), the left-handed helical structure is irradiated by left-handed CPL, and the similar helix locations have the strongest optical chirality enhancement but different signs for the two polarizations. Therefore, the total enhancement is small. However, the left-handed helical structure is irradiated by the right-handed CPL, and the enhancement almost vanishes.

Figure 1.16 Calculated chirality enhancements for a left-handed helix irradiated with (a) LCP and (b) RCP at a wavelength of 2.03 μm. The response almost vanishes when illuminated with RCP.\textsuperscript{[22]}

Unlike a single helix, a multiple helical structure is more complex because each helix interacts with others. For a multiple helical structure, a comparison of helices with different pitch, radius and wire diameter are shown in Figure 1.17. However, the optical chirality of a bigger structure is decreased by a factor of ~1.7 from a smaller helical structure.
Figure 1.17 Optical chirality map of four helices with pitches of (a) 100 nm and (c) 2.0 um. Strong chiral near-fields are generated in four-helical metamaterials with pitches of 100 nm. (b) and (d) cross sections of four-helices exhibit confinement to the inner region.[23]

From a chemical point of view, stereoisomers describe materials with the same components but different spatial arrangements of atoms or molecular subgroups within molecules. Analogically to stereoisomers, in the nanotechnology field, metamaterials with the same constituents but different spatial arrangements are named stereometamaterials and can also tailor optical chirality responses.

Figure 1.18 shows that enhanced optical chirality was obtained when two split-ring resonators were twisted and stacked. Note that the strongest enhancement of optical chirality in the left structure happened when it was irradiated with RCP, not LCP. The strongest enhancement is in the gap between the two resonators.
Figure 1.18 Optical chirality enhancement induced by stereometamaterial under (a) LCP and (b) RCP illuminated at a wavelength of 1.34 um. [22]
Our group has been focusing on helical structures in fabrication and simulation for many years. Figure 1.19 shows the distribution of the scattering electric field of a three-turn left-handed AgNH irradiated by a 360 nm (UV) LCP and a 500 nm (visible) LCP. A plot of the integrated scattering intensity ($|E_{sca}|^2$) normalized by the incident intensity as a function of the radius of AgNH cross section is shown in Figure 1.19 (d). Therefore, more UV light prefers locating inside AgNH, but more visible light than UV light is scattered. The results illustrate that the optical responses of AgNH are different under different wavelength radiations.

Figure 1.19 (a) A left-handed AgNH intersected by a red sheet. The scattering electric field ($E_{sca}$) is in the red sheet region, with an incident wavelength of (b) 360 nm and (c) 500 nm. (d) The ratio of $|E_{sca}|^2$ per $|E_0|^2$ versus $r$ (the radial axis pointing from the center of the red sheet, as inset in (b, c)). The diameter ($r$) of AgNH is 37.5 nm.[24]
1.4 Enantiodifferentiation by interacting with plasmonic nanostructure

1.4.1 Plasmonic CD induced by enantiomers

Enantiodifferentiation can be achieved by induced CD of achiral nanoparticles. The plasmonic CD of achiral Au nanoparticles was induced when chiral molecules were close to the Au nanoparticle surface without bonding between the chiral molecules and achiral gold particles. The authors control the induced CD by controlling the distance between the chiral molecules and Au, mainly derived from the Coulomb interaction between the plasmon and chiral molecule. This is due to optical absorption from the chiral currents, inside which Au nanoparticles are induced by a dipole of these molecules. The induced CD is very sensitive to the chiral molecule thickness and the diameter of Au particles. The induction quickly decays when the molecule–Au distance is over 10 nm. This method is promising for enhancing the sensitivity of chirality detection. They can analyze molecular information using induced CD.
Figure 1.20 (a) Experimental scheme. Pristine Au is covered with a ~20 nm mixture comprised of PMMA and riboflavin. (b) Absorption and (c) CD spectra of pristine Au islands (black solid line), Au after film removal (black dotted line), Au islands + PMMA film (red line), island + PMMA + riboflavin (blue line), PMMA + riboflavin (green line).[25]

Detecting hot spots between closely spaced nanostructures is also an important method for plasmon-enhanced circular dichroism signals. Maxim L. Nesterov and co-authors demonstrated...
that enhancements of roughly three orders of magnitude were calculated in interactions between a chiral medium and an achiral nanostructure, as shown in Figure 1.21. The absorption peak of the chiral molecule corresponds to the CD peak at a wavelength of 200 nm. Because the chiral media are located at the gap, they observed a strong induced plasmonic CD signal at a wavelength of ~780.

Figure 1.21 (a) Chiral media located on hot spots of achiral nanorod arrays. The nanorod measurements are 159 nm in length, 20 nm in width, 40 nm in height and with a 650 nm period. The inset in (b) shows the chiral media located at the hot spots. (b) Absorption spectra of chiral molecules without nanostructures (thin grey line) and with nanostructures (thick black line). (c) CD spectra of chiral molecules without nanostructures (thin orange line) and with nanostructures (thick orange line). Left scale: absolute values; right scale: CD in medg. (d) \( EF_{CD} \) is the ratio of total CD divided by the isolated chiral medium. [26]

The stronger near field plays an important role in enhancing CD spectroscopy. Therefore, the authors quantitatively analyzed the effect of chiral medium volume and distance between arrays on enhancement. The gap antenna shows that maximum enhancement factor (EF) reaches 3000 when the gap distance is 5 nm. However, if the gap distance is too large, they can regard this system as equivalent to the single-rod configuration. The CD enhancement factor not only strongly
depends on the chiral medium volume, but also on the gap distance. This work only shows the results from a simulation, because they are challenging to achieve and apply to the device.

![Figure 1.22](image)

Figure 1.22 Plots of CD enhancement factor as a function of (a) chiral medium volume and (b) gap distance. \([26]\)

### 1.4.2 Differential plasmonic optical activity change in left-/right-handedness structures induced by proteins

To the best of my knowledge, only one study by Kadodwala et al. reports on the interaction of achiral molecules with chiral nanostructure. Plasmonic CD was generated on the surfaces of planar Au gammadions to differentiate the handedness of specific higher-order proteins.\([14]\) Bio-enantiomers generally absorb UV light, leading to optical mismatches with the visible plasmonic CD of planar Au gammadions. Optical mismatching gives rise to a shift in CD peaks without an apparent change in intensity. The change in enantiomer chirality causes the CD peaks to shift in opposite directions, resulting in enantiodifferentiation. The mechanism of enantiodifferentiation remains ambiguous.
The CD spectra of right- and left-handed gammadion arrays are shown in Figure 1.23. The gammadion arrays’ chiral response is in the range of 500~850 nm with three LSPR modes of Label I, Label II and Label III.

Figure 1.23 (a) Right-handed gammadion arrays. SEM images of (b) an achiral cross, (c) right-handed gammadion and (d) left-handed gammadion. They labeled these three models Label I, Label II and Label III, respectively (e) The CD spectra of left-handed and right-handed gammadion arrays immersed in DI water. [14]

LSPR is very sensitive to its surrounding medium. Thus, with an increasing dielectric constant in the surrounding environment, LSPR could be redshifted. The LSPR spectral shift in response to changes in refractive index can be described as

\[ \Delta \lambda = m \Delta n [1 - \exp \left( -2d/l_d \right)] \]

where \( m \) is a sensitivity factor depending on the nanoparticle structure, \( \Delta \lambda \) is the change in the effective refractive index induced by molecules close to metallic surfaces, \( d \) is the effective thickness of the adsorbate layer and \( l_d \) is the spatial evanescent decay of the local fields. The quantity \( m \) is the sensitivity of the nanomaterial when it changes in the local refractive index, which will be different for each LSPR mode.
Plasmonic planar chiral metamaterials can generate superchiral light under normal CPL radiation. Superchiral light means a “twist” on a shorter length than CPL at the same frequency. This holds promise for enhancing the sensitivity of chiral molecule detection. In this paper, several α-helical and β-sheet secondary structure proteins have been studied. When β-lactoglobulin (β-sheet) is absorbed on Au gammadion arrays, the resonance peak of right-handed gammadion shows a red shift, but an obvious blue shift has been found in left-handed gammadion arrays. These different chiral responses have been observed for left- and right-handed planar Au gammadions, resulting in enantiodifferentiation. However, no significant change is observed for α-helical secondary structure proteins in the CD spectra, no matter whether left- or right-handed structures. Moreover, if β-lactoglobulin is heat-treated, meaning that the β-structure is destroyed, a smaller difference in peak shift is observed. This method could be used to detect whether a β-structure is destroyed. However, for this case, until now, the mechanism has not been clear. The authors believe that the different responses of the right- and left-handed gammadions after absorbing β-sheet proteins are caused by quadrupolar contributions to optical activity. The superchiral light generated by gammadion arrays displays steep field gradients, which will increase quadrupolar contributions to the optical activity related to the dipolar contributions. However, α-helices in the adsorbed state show broad spatial distribution, which will be isotopic distribution from a surface perspective. Therefore, one expectation is that the quadrupolar contribution to the dissymmetry is small. However, for β-sheet secondary structure proteins, which shows a structure with anisotropy of the adsorption layer, and this facilitates the large quadrupolar enhanced optical activity. In summary, superchiral electromagnetic fields generated by planar Au gammadion structures are a new method that can be used for biosensing.
In 2015, this group published another very similar work on detecting ligand-induced conformational changes in protein. The “shuriken” structure can generate chiral evanescent files that exhibit “superchirality,” which can “twist” on a shorter length than CPL under the same frequency. The experimental results proved that the superchiral electromagnetic field is sensitive to changes in higher-order (tertiary and quaternary) protein conformation. Figure 1.25 shows the scanning electron microscopy (SEM) image (left-handed) and optical rotatory dispersion spectra of a pair of shuriken nanostructures.
They selected two proteins of 5-enolpyruvylshikimate 3-phosphate synthase (ERSPS) and Shikimate kinase (SK) that are induced by a ligand, which results in a conformational change. To quantitatively evaluate the enantiodifferentiation effect, they defined $\Delta \Delta \lambda$ as the asymmetry in the refractive index of the surrounding medium. $\Delta \Delta \lambda$ stands for the difference between $\Delta \lambda_R$ and $\Delta \lambda_L$ ($\Delta \lambda_{L/R}$ is the resonance wavelength shift for LH and RH chiral structures). Significant negative $\Delta \Delta \lambda = \Delta \lambda_R - \Delta \lambda_L$ values are calculated by ORD spectra, as shown in Figure 1.26. Both ERSPS and SK induce large positive $\Delta \Delta \lambda$ values in the presence of protein only. However, if the proteins are exposed to ligands, the ligand-induced conformation changes from an open to a closed form. Thus, negative $\Delta \Delta \lambda$ values can be observed. In this work, it was also noted that the chiral nanostructures exhibit steep field gradients, which can enhance any quadrupolar contributions compared to dipolar contributions. This method can quickly detect ligand-induced tertiary and quaternary changes in protein structure.
In general, chiral nanostructures can be classified into two main types. One includes chiral nanostructures with a handed shape; the other is configurational chirality, which denotes arranged identical achiral particles in a handed fashion. The handed character collective plasmonic resonance is formed along the entire nanostructure, the response of which is associated with plasmonic nanoparticles with large polarizability. The handed structure is more suitable for the enantiodifferentiation in this study. I thus focus on 3D helical structures.
1.5 Fabrication of Helical Nanoparticles

A series of fabrication approaches have been reported. First, achiral nanoclusters have been grafted with chiral ligands to create helical atom patterns on nanoclusters.[28] Second, helically twisted layer-by-layer structures have been generated using photolithographic techniques in which each layer is composed of a periodic array of plasmonic nanoparticles (NPs).[29] Third, plasmonic NPs have been helically assembled on helical templates (e.g., DNA, peptides, chiral mesoporous silica, inorganic nanohelices, organic spiral fibers[30] and chiral nematic films of cellulose nanocrystals[31, 32]). Fourth, helical structures have been generated without chiral ligands or helical templates, by means of direct laser writing into positive-tone photoresists followed by electrochemical deposition of gold,[33] radio-frequency plasma prior to electroless plating,[34] multi-beam holographic lithography,[35] colloidal nanohole lithography,[36] focused ion beam-induced deposition, electron beam-induced deposition[37] and glancing angle deposition (GLAD).[38, 39] In my dissertation, I focus on 3D helical structures.

1.5.1 Combination of direct laser writing and electrochemical deposition

Very similar helical structures with different chirality responses fabricated by direct laser writing combined with electrochemical deposition are shown in Figure 1.27. First, the photoresist (the blue cube) was coated on indium tin oxide (ITO) glass (green substrate). Second, after direct laser writing inside the photoresist, an polymer block array was fabricated. I then removed the block via plasma etching and the Au helix arrays were exposed to air. The gold helices exhibit that the collective plasmonic modes extend for the entire structure.
1.5.2 Template-assisted electrosynthesis (TSE)

Another way to generate metallic nanohelices is template-assisted electrosynthesis. First, gold nanorods (AuNRs) are electrodeposited in anodized aluminum oxide (AAO) nanochannels, then Pd/Cu nanorods are synthesized by electrochemical co-deposition. Pd/Cu nanorods are deposited on the top of AuNRs in a plating solution (Figure 1.28(a)). Second, Cu is selectively etched in the Pd/Cu NR to produce Pd NH (Figure 1.28(b)). Third, the gold is deposited into the empty spaces between the PdNHs of the pitches (Figure 1.28(c)), then the Pd is selectively dissolved to create Au NH (Figure 1.28(d)).
1.5.3 Combination of stimulated-emission depletion and inspired direct laser writing

With the development of fabrication technology, Au triple-helices are achieved by nesting three single helical structures in one another. This fabrication technique combines stimulated-emission depletion (STED) and inspired direct laser writing (DLW). The fabrication process is shown in Figure 1.29. First, a polymer template is written on conductive but transparent ITO glass using an STED-DLW device. Second, electrochemical deposition is used to fill three voids in the polymer templates with gold. Third, oxygen plasma is used to remove the polymer templates, then the gold triple helix is formed.
There is another method for fabricating helical structures using a bottom-up technique. This technique focuses on beam induced deposition, which is a one-step fabrication technique. The fabrication process involves several interactions between the incident ion beam, substrate charge, scattered particles and nanostructure. The above parameters must be controlled very precisely to produce the helical structure. However, in the presence of a strong proximity effect from nanohelices located close to one another, the pitch decreases as the pitch number increases. The dimensional uniformity is poor. In 2014, Marco Esposito et al. explored the surface charge effects
of a variety of substrates with different electrical properties and effectively controlled the proximity compensation by studying charge effects. They achieved accurate dimensional control and nano-level resolution in the manufacture of chiral helical structures.

Figure 1.30 Focused ion beam induced deposition. SEM image of the chiral nanostructure (5 turns with width \( \sim 80 \) nm, pitch \( \sim 200 \) nm and height \( \sim 280 \) nm).

1.5.4 Colloidal nanohole lithography

Another helical structure fabrication technology is called “hole-mask colloidal nanolithography.” It is used to fabricate helical-type ramp structures over a large area of 1 cm\(^2\). Compared with other manufacturing technologies, hole-mask colloidal nanolithography is a large-area manufacturing technology, with important applications. For this case, the structure and handedness of helical nanoparticles can control the incident angle, rotation speed and rotation direction. The helical nanoparticles have a diameter of about 260 nm and their width shrinks from roughly 90 nm to about 20 nm. This technology is similar to GLAD.
Figure 1.31 Colloidal nanohole lithography and incident angle rotation evaporation creating 270° left- and right-handed helical structures. SEM images of nanoparticles generated by (b) left-hand rotation and (c) right-hand rotation. The inset scale bar is 1 um. [36]

1.5.5 Glancing angle deposition

Our group has been studying the chiral optical responses of Ag helices generated by GLAD for many years. Figure 1.32 shows SEM images of the typical chiral structure silver nanohelices with left and right handedness as a function of pitch number.[24] CD spectra of LH/RH-AgNH arrays with tailoring the n are shown in Figure 1.32(g). The CD spectra are composed of bisignated peaks, one in the UV regime (longitudinal surface plasmon resonance) and the other in the visible regime (transverse surface plasmon resonance). The chiroptical activity in the UV region barely varies with the increasing number of pitches, in terms of the CD intensity and LSPR peak position, because the diameter of AgNH seldom changes. Unlike in the UV region, in the visible region, an increase in pitch number significantly decreases the intensity of CD and causes an obvious LSPR
blueshift. This indicates that the mechanism of chiroptical activity in the UV regime is different from that in the visible regime. UV radiation is mainly absorbed inside silver, but visible light is mainly scattered by silver. Meanwhile, the simulation is also carried out.

Figure 1.32 Cross-sectional SEM image of a silver nanohelix as a function of pitch: homochiral Ag nanohelix arrays, with left-handedness (a, c, e) and right-handedness (b, d, f), Ag helix with pitch ~200 nm with a pitch number (n) of 1 (a, b), 2 (c, d), or 3 (e, f). (g) CD spectra of homochiral Ag helix as a function of pitch number. The CD spectra changes sign while the incident radiating direction in the visible region switches.

They also studied more complex structures based on a single helix, and a combination of LH and RH helices to create heterochiral bi-axial Ag nanohelices, with which two different incorporated helical axes are shown in Figure 1.33. The CD spectra changes sign while the incident radiating direction in the visible region switches.
In summary, the mechanism of template-assisted electrosynthesis (TSE) is not clear so far. For FIBID, it is difficult to fabricate a helix with a small pitch. Other methods involve multi-step preparation processes, so there is a high risk of contamination during the fabrication process. In practical applications such as optical devices, nanostructures that often require large areas and less contamination are required. Superior to other helix-fabrication techniques, GLAD provides one-step, wafer-scale production of helical metamaterials on various kinds of substrates. Therefore, GLAD is the best method to study the interaction between nanohelical structures and molecules.
2 Experiment and Characterization Methods

2.1 Glancing angle deposition

The GLAD technique is a combination of oblique angle deposition and azimuthal rotation of the substrate. A typical GLAD system and two important angles are shown in Figure 1.3a, where deposition angle $\alpha$ is the angle between the incident vapor flux and the substrate normal, and substrate rotation angle $\varphi$. During the deposition process, the nonplanar surface will exhibit the ballistic shadowing, which prevents the incident flux from reaching the shadowed regions. Nuclei will initially form randomly at the beginning of the deposition, and the shadowing effect causes the incoming atoms condense on the nuclei rather than in the shadowed region (Figure 2.1b). As the vapor flux comes continuously, the shadowing effect the dominants and leads to the formation of sculptured thin film composed of separated tilted helix.[44, 45] During GLAD, the clockwise/counterclockwise rotation of substrates gives a rise to the deposition of right/left-handed nanohelical structure (RH-NHs and LH-NHs).

![Figure 2.1](image.png)

Figure 2.1 (a) Schematic of GLAD process. The vapor from PVD source evaporated to the substrate which deposition angle ($\alpha$) is larger than 75 °. (b) GLAD-induced ballistic shadowing of the random atoms. The subsequent flux are deposited onto the nuclei instead of the shadowed region.[44-46]
2.2 Fabrication of helical nanoparticle by GLAD

AgNHs: In a custom-built GLAD system (JunSun Tech Co. Ltd, Taiwan) was applied to generate 3D plasmonic NS arrays on a large area substrate. The chamber interior is generated a high vacuum of $10^{-7}$ to $10^{-6}$ Torr by a cryo pump. In this report, the deposition angle in plasmonic nanospiral fabrication is $86^\circ$. Ag pellets (99.99%, Kurt J. Lesker) were evaporated at a rate of ~0.3 nm/s monitored by a quartz crystal microbalance (QCM) using an electron-beam accelerating voltage of ~8.0 kV and emission current of 15–25 mA. Ag was deposited on sapphire (MTL Hong Kong) and Si wafer (Semiconductor Wafer, Inc.) substrates over an area of 1.5×1.5 cm². During deposition, an ethanol/water cooling system was used to control substrate temperature at roughly 0 °C. The deposited Ag was sculptured to form 1R-AgNHs, 1L-AgNHs and tilted nanorods. To produce 1R/L-AgNHs, GLAD was operated at a deposition angle of $86^\circ$ with respect to the substrate normal, and the substrate was rotated clockwise/counterclockwise at a rate of 0.12°/s for a full circle. To produce the tilted nanorods, the deposition angle was set to 85° and the substrate was fixed.

AgHNPs: Under some experimental condition above, to produce RH/LH-Ag NPs-P(x), the substrate was fastly rotated clockwise/counterclockwise at a rate $R_r$ (in units of degrees per second, or °/s) given by

$$R_r = 360 \frac{R_d}{P} \quad (2.1)$$

where $R_d$ is the deposition rate on the substrate surface calibrated as 0.045 nm s⁻¹, and $P$ is the helical pitch. To make $P$ decrease from 80 to 17 nm, $R_r$ was controlled to increase from 0.2 to 1.0 °/s, according to Equation (2.1). The nominal $P$ was calibrated by

$$P = \frac{H}{n} \quad (2.2)$$

where $H$ is the helix height controlled to be roughly 100 nm, and $n$ is the number of helical pitch equal to how many circles the substrate was rotated in.
At the deposition angle of $0^\circ$ and $T_{\text{sub}}$ of $\approx 0$ °C, a substrate that was not rotated was deposited with 10 nm thick Ag, leading to the generation of AgNPs without hidden chirality.

**Chiral Host @ Achiral Guest NPs:** The host of chiral NPs was made from Ag and Cu, that of the chiral host was operated at $\alpha$ of $86^\circ$, $T_{\text{sub}}$ of $\approx -40$ °C, and a deposition rate of 0.3 nm s$^{-1}$ monitored by the QCM, using an electron-beam accelerating voltage of 8.0 kV and emission current of 15–25 mA for Ag pellets (99.99%, Kurt J. Lesker) and 30–40 mA for Cu pellets (99.9999%, Torsh Technology Limited). Without substrate rotation, the guest including Cu, Ag, and Au (99.999%, Kurt J. Lesker) was deposited at $\alpha$ of $0^\circ$, $T_{\text{sub}}$ of $\approx -40$ °C, and Rd of 0.1 nm s$^{-1}$. It was used an electron-beam accelerating voltage of 8.0 kV and emission current of 22 mA for Cu, 16 mA for Ag, and 60 mA for Au. The nominal thickness of the guests was controlled in a range of 0–30 nm, monitored by the QCM. To study the host oxide effect, after the GLAD of the chiral host, the samples were sufficiently exposed in the ambient environment for spontaneous oxidation before the coating of the achiral guest. The host (chiral CuHNPs and AgHNPs) was immersed in dimethyl sulfoxide (DMSO, anhydrous, $\geq 99\%$ RCI Labscan) dissolved with 0.334% w/w PMMA (ACROS Organics, average MW of 35 000 g mol$^{-1}$) overnight, in a vacuum of $(-19)$–$(-25)$ in. Hg. The PMMA-treated samples were sufficiently rinsed with DMSO, resulting in the conformal coating of the host with a $\approx$ 3 nm thick PMMA layer. Then, without substrate rotation, the PMMA-coated host was deposited with the guest at $\alpha$ of $0^\circ$, $T_{\text{sub}}$ of $\approx -40$ °C, and Rd of 0.1 nm s$^{-1}$.

### 2.3 Interaction between the AgNHs and molecules

**Water effect:** A homemade liquid cell (with a path length of 1 mm and volume of approximately 0.08 ml) was used to evaluate the effect of aqueous solvent on the chiroptical activity of a sample. First, a sample deposited on sapphire was etched in 5% HF for 15 s to remove surface oxides/contaminants, and then sufficiently rinsed with DI water (18.2 MΩ, Milli-Q reference water purification system fed with campus distilled water) and dried with N$_2$. Second, the HF-treated sample was immediately transferred into the liquid cell to measure the CD and extinction spectra. Third, 0.08 ml of DI water was injected into the cell to completely immerse the sample in DI water.
(i.e., the wetting process), and then the CD and extinction spectra were recorded. Fourth, DI water was completely removed from the cell by sufficiently drying with N₂ (i.e., the drying process) to record CD and extinction spectra. Fifth, multiple alternating wetting and drying processes were applied to study the reversibility of the aqueous solvent effect at the same spot on a sample.

**Alkyl ligands and AgNHs interaction:** The interaction between AgNHs and alkyl ligands, including octane (≥ 99.0%, Sigma), nonanoic acid (≥ 97%, Sigma), octylamine (99%, Aldrich), and octanethiol (≥ 98.5%, Aldrich) in liquid, was evaluated in two steps. First, a reference CD of a pristine AgNH array deposited on a sapphire substrate was recorded. The array was then immersed in liquid C8-G (2 mL) for 16 h. The grafted array was rinsed with ethanol and then dried with N₂ to completely remove the physically adsorbed C8-G. For octane (C8-H), the array was directly dried with N₂ after grafting without solvent rinsing. The grafted array was then characterized by CD.

**L- and D-GSH and AgNHs interaction:** L- and D-GSH (98 %, GL Biochem Shanghai Ltd.) were dissolved in an aqueous buffered solution (0.1 mol/L citric acid and 0.2 mol/L Na2HPO4, pH of ~3) with concentration of 1 or 10 μmol/L. To study the chiroplasmon-induced GSH differentiation, was evaluated in three steps. First, a reference CD of a pristine AgNH array deposited on a sapphire substrate was recorded. Second, the array was then immersed in 10 μmol/L GSH for 1 hr. Third, the grafted array was rinsed with buffer and then dried with N₂ to completely remove the physically adsorbed GSH. The grafted arrays was then characterized by CD again.

**Enantiomers and hidden AgNHs interaction:** Enantiomers (1 and 2) were dissolved in ethanol: CH₂Cl₂ (9:1, volume ratio) with a concentration of 10 mmol/L. The hidden AgNHs spontaneously undergo oxidation under ambient conditions and were covered with thick silver oxides. To avoid the oxidation-induced deterioration of the enantiomeric grafting, the freshly deposited AgHNPs were immersed in the enantiomeric solution for 16 hours at roughly -4 °C. Then the treated sample was sufficiently rinsed with the mixture solvent and dried with N₂ to completely remove the physically absorbed enantiomers. To study the solvent effect on the plasmonic optical activity, the AgHNPs were immersed in the mixture solvent for 16 hours at -4 °C, followed by drying with N₂.
2.4 Characterization

*Measurement of UV–Visible Extinction and CD Spectra of AgNHs:* CD was monitored in transmission mode (Olis 1000 CD), under circularly polarized incident light along the substrate normal. A sapphire substrate with deposited AgNHs was rotated clockwise at 0.1 rpm to monitor CD in the wavelength range of 300–700 nm to eliminate linear birefringence. Five spectra were subsequently recorded and algebraically averaged to obtain a CD spectrum of a sample.

*Measurement of UV–Visible Extinction and CD Spectra of Hidden AgNHs:* Bio-Logic CD (MOS 500) was used to monitor UV–visible extinction and CD spectra of the samples deposited on sapphire, under an irradiative incident along the substrate normal. The measurement was ambiently operated. To eliminate linear birefringence, the samples were continuously rotated clockwise at 0.2 rpm to monitor a CD spectrum in a λ range of 200–750 nm. Four CD spectra were subsequently recorded and algebraically averaged to obtain a CD spectrum of a sample.

*Measurement of water contact angle:* A 2-µl droplet of DI water was applied to a sample to measure the contact angle using a contact angle meter (CA100A, Innuo Shanghai).

*Structure Characterization:* The as-deposited samples were mechanically split, leaving the freshly exposed surfaces for the characterization of SEM (Oxford, LEO 1530). The AgHSs were scratched off the substrates and well dispersed in ethanol via ultrasonication for 5 min. Several drops of the mixture were applied to a lacy carbon film on a grid structure (Electron Microscopy Sciences). The grid was dried in ambient and inspected by TEM with low resolution (Tecnai G2 20 STWIN) and high resolution (Tecnai F20 microscope, FEI, 200 kV; a CM-120 microscope (Philips, 120 kV). XPS (Sengyang SKL-12, nonmonochromatic Mg Kα radiation of 1253.6 eV, at a current of 15 mA, voltage of 10 kV, takeoff angle (between the sample and detector) of 90°, and in a vacuum of ≈2 × 10⁻⁹ mbar). The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy at an incident angle of 45° (PerkinElmer Spectrum Two) with a horizontal ATR accessory (germanium crystal and DTGS detector, PIKE Technologies). Without or with the enantiomeric grafting, the AgHNPs deposited on sapphire were characterized by Fourier transform infrared spectroscopy (FTIR, PerkinElmer Spectrum Two). The enantiomeric solution with a
concentration of 10 mmol/L was applied to KBr overnight, which was monitored by FTIR spectroscopy to study the enantiomeric vibrations.
3 Enantioselective Weakening Circular Dichroism Plasmonic Nanoparticles Induced by Surface Grafting with molecules

3.1 Introduction

Plasmons with chiroptical activity can be also generated by the molecule-free fabrication of planar chiral metamaterials,[14, 48, 49] layer-by-layer chiral stacking,[31, 50-53] and three-dimensional (3D) chiral metamaterials.[33, 36, 54-57] Considering the great achievements in the bioapplications derived from molecule–plasmon interactions, it is intuitive to ask how chiral and achiral molecules interact with intrinsic plasmons that originate from chiral structures of plasmonic materials without conjugation with chiral molecules. Such knowledge may aid the development of chirality-related bioapplications. Despite some simulation studies,[15] there is only one experimental report on the dissymmetric interaction of chiral supramolecules and planar gold (Au) gammadions, which occurs when supramolecules have optical absorption that is off resonance with the chiroptical activity of Au gammadions.[14]

3.2 Weakening plasmonic circular dichroism of AgNHs induced by grafting with alkyl ligands

3.2.1 Result and Discussion

Given the chirality-related complexity in chiral molecule–plasmon interactions, it is a prerequisite to understand achiral molecule–plasmon interactions.

In this chapter, my study was divided into two parts. I first studied the interaction of alkyl ligands (CH₃(CH₂)₆CH₂-G or C₈-G, where G is –H, –COOH, –NH₂ and –SH) and plasmons excited from silver nanospirals (AgNHs) by quantitatively evaluating the change in circular dichroism (CD) of AgNH arrays induced by grafting the alkyl ligands on the AgNHs and then we studied more complex chirality-related interaction that is chiral molecule–AgNHs interactions.
C8-G and AgNHs were chosen for the following reasons. First, self-assembled monolayers (SAMs) of alkyl ligands on noble metals and the binding nature of diverse Ag-G contacts have been widely studied. Second, plasmonic NHs are an emerging 3D chiral metamaterial that have an intrinsic chiroptical response decoupled from supporting substrates and tend to possess chiroptical activity stronger than that of planar chiral metamaterials. Third, Ag has higher plasmonic quality than Au. Despite the well-known plasmonic degradation of Ag caused by the inevitable surface sulfidation and oxidation, AgNH arrays tend to retain strong chiroptical activity for at least 3 months (Figure 3.1). Therefore, AgNHs with high chiroptical stability are suitable to study molecule–chiral nanostructure interactions.

![Figure 3.1](image)

Figure 3.1 (a) Cross-sectional SEM image of a 1LH-AgNH array with a helical pitch of ~200 nm. Inset: Cross-sectional SEM image of a 1LH-AgNH with a scale bar of 200 nm. (b) CD spectra of a 1LH-AgNH array as a function of ambient aging duration. The CD spectra barely degrade, indicating excellent chiroptical stability.

On a flat substrate, glancing angle deposition (GLAD) enables the formation of a close-packed array of one-pitch AgNHs with a uniform helical pitch \( P \), inset of Figure 3.2b) of ~200 nm, wire diameter \( d \) of ~45 nm, and right-handedness (i.e., 1RH-AgNHs where “1” represents one pitch, Figure 3.2a) and left-handedness (i.e., 1LH-AgNHs, Figure 3.1a). Chiroptical activity of the AgNH arrays was characterized by CD in the UV-visible region, with wavelength \( \lambda \) of 300-700 nm. To eliminate linear birefringence, the sample was continuously rotated during CD measurement. The
CD spectrum is composed of two peaks separated at $\lambda$ of 400 nm, with sign opposite one another (Figure 3.2b).

![Figure 3.2](image)

Figure 3.2 (a) Cross-sectional SEM image of a close-packed array of 1RH-AgNHs deposited on a Si wafer. Inset: SEM image (scale bar: 100 nm) and schematic diagram of an as-deposited 1RH-AgNH deposited on sapphire. (b) CD spectra of an array of 1RH-AgNHs (blue line) and 1LH-AgNHs (red line). Inset: schematic diagram of a 1RH-AgNH (in blue) and 1LH-AgNH (in red) with a helical pitch (P) and wire diameter (d). “T” and “L” are denoted the transverse and longitudinal plasmonic mode, respectively.

The peak in the UV region is attributed to the plasmonic transverse (T) mode, and another in the visible is the plasmonic longitudinal (L) mode. The CD spectrum flips around the zero-CD axis while the helicity of AgNHs is switched. When Ag nanostructures lack in the helicity and appear to be nanorods (Figure 3.3a), the chiroptical response disappears (Figure 3.3b). It is illustrated that the chiroptical activity intrinsically stems from the structural helicity. Note that GLAD can provide the AgNH arrays with reproducible chiroptical activity (especially for the T-mode; see Figure 3.4), allowing reliable investigation of the molecule–chiral nanostructure interaction. The AgNH array is too thick to monitor an extinction spectrum.
Figure 3.3  (a) Cross-sectional SEM image of slanted Ag nanorods deposited by GLAD. (b) CD spectrum of an array of slanted Ag nanorods on sapphire.

Figure 3.4 The grafting of C8-G on 1RH-AgNHs characterized by CD: G of (a) -SH, (b) -NH₂, (c) -COOH, and (d) -H; pristine 1RH-AgNH arrays deposited on sapphire (black lines); the
arrays grafted with C8-G (other colors). $\lambda_{\text{max},0}$ is the wavelength at which a pristine 1RH-AgNH array has maximum absolute amplitude of a CD peak.

Octane and its derivatives (C8-G) mainly absorb UV light with $\lambda < 280$ nm (Figure 3.5a), and do not display detectable chiroptical activity (Figure 3.5b).

![Figure 3.5 (a) UV absorption and (b) CD spectra of 0.01 mol/L C8-G (G: -H, -COOH, -NH2, -SH) dissolved in ethanol.](image)

C8-H tends to physically adsorb on AgNHs, and the other derivatives are grafted onto AgNHs via the formation of Ag-G contacts (Figure 3.6). Figure 3.6a shows that the grafting of C8-SH causes $\nu$(S-H) at 2574 cm$^{-1}$ to disappear, illustrating the formation of Ag-S contacts. ATR-FTIR shows that the grafting of C8-NH2 causes $\delta$(N-H) to shift from 1567 to 1595 cm$^{-1}$ (Figure 3.6b) because of the formation of Ag-NH2 contacts, and the grafting of C8-COOH eliminates $\nu$(O-H) at 3746 cm$^{-1}$ (Figure 3.6c), which is ascribed to the generation of Ag-OOC contacts. Detection of $\nu$(C-H) at 3000–2850 cm$^{-1}$ demonstrates the physical adsorption of C8-H on AgNHs (Figure 3.6d).

Despite off resonance of the C8-G optical absorption and the chiroptical activity of a 1RH-AgNH array, the grafting of C8-G generally lowers the CD amplitudes of the plasmonic T- and L-modes (Figure 3.4).
To quantitatively evaluate the chiroptical weakening effect, the interaction index $\Delta CD\%$ with respect to the wavelength $\lambda_{max,0}$ at which the plasmonic CD modes of a pristine 1RH-AgNH array has maximum absolute amplitude (Figure 3.4a) can be calculated by,

$$\Delta CD\% = \frac{CD_m - CD_o}{CD_o} |\lambda_{max,0}| \times 100\% \quad (3.1)$$

where the subscript “m” and “0” represent a 1RH-AgNH array with and without the grafting of C8-G, respectively. Multiple measurements were obtained and $\Delta CD\%$ was statistically evaluated to have an algebraic average value (summarized in Table 3.1).
Table 3.1  Summary of the chiroptical weakening effect of 1RH-AgNHs induced by the grafting of C8-G.

<table>
<thead>
<tr>
<th>Alkyl ligands</th>
<th>BE of Ag-G (eV)</th>
<th>$\varepsilon_r^m$</th>
<th>T-mode ($\lambda_{max,0}$ of ~370 nm)</th>
<th>CD</th>
<th>L-mode ($\lambda_{max,0}$ of ~560 nm)</th>
<th>$\varepsilon_r^{air:Agx0}$/$\varepsilon_r^{air:Agx0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta CD$% (%)</td>
<td>$\Delta \lambda_{max}$ (nm)</td>
<td>$\Delta CD$% (%)</td>
<td>$\Delta \lambda_{max}$ (nm)</td>
</tr>
<tr>
<td>C8-H</td>
<td>~0</td>
<td>1.96</td>
<td>-4.9 ± 0.4</td>
<td>1</td>
<td>-4.1 ± 0.1</td>
<td>1</td>
</tr>
<tr>
<td>C8-COOH</td>
<td>~0.2</td>
<td>2.48</td>
<td>-19.5 ± 5.2</td>
<td>-1</td>
<td>-13.9 ± 1</td>
<td>-9</td>
</tr>
<tr>
<td>C8-NH$_2$</td>
<td>1.64</td>
<td>3.58</td>
<td>-30.0 ± 5.4</td>
<td>-3</td>
<td>-20.5 ± 6.3</td>
<td>-14</td>
</tr>
<tr>
<td>C8-SH</td>
<td>3.35</td>
<td>3.95</td>
<td>-34.5 ± 3.2</td>
<td>-1</td>
<td>-26.1 ± 2.6</td>
<td>-7</td>
</tr>
</tbody>
</table>

The chiroptical weakening of the two modes causes $\Delta CD$% to have negative signs, and is exacerbated with increasing bond energy (BE) of the Ag-G contacts (~0 eV for the physical adsorption of C8-H, ~0.2 eV for Ag-OOC,$^{[60, 61]}$ 1.64 eV for Ag-NH$_2$,$^{[62]}$ and 3.35 eV for Ag-S.$^{[63]}$). The weakening effect of the T-mode is larger than that of the L-mode (Figure 3.7a).
Figure 3.7 Chiroptical weakening induced by the grafting of C8-G on 1RH-AgNHs. (a) Plot of interaction index ΔCD% versus bond energy (BE) of the Ag-G contacts. (b) Plot of $\varepsilon_{\text{air}:\text{m}^{\text{Ag},\text{O}}}/\varepsilon_{\text{air}:\text{m}^{\text{Ag},\text{G}}}$ versus $\varepsilon_{\text{m}}$. Black squares and red circles represent the plasmonic T- and L-mode, respectively. Note that an analogous chiroptical weakening effect occurs upon the grafting of C8-G onto the 1LH-AgNH arrays (e.g., the grafting of C8-COOH, Figure 3.8).

Figure 3.8 The grafting of C8-COOH on 1LH-AgNHs characterized by CD: a pristine 1LH-AgNH array deposited on sapphire (black line); the array grafted with C8-COOH (blue line).
Simultaneously, the grafting of C8-G causes the two modes to blueshift, and the L-mode tends to blueshift more obviously than the T-mode (Table 3.1). Note that in this work the molecule-nanoparticle interaction is characterized by monitoring CD spectra, different from the typical characterization using UV-visible absorption/extinction spectra. Usually, however, the two spectra tend to coincide in resonance shift and amplitude change. It has been widely studied the grafting of achiral ligands (terminated with –COOH, –NH2 and –SH) on achiral nanoparticles, revealing that the interaction sensitively depends on plasmonic materials, nanoparticle shape and size, surfactants, and ligands in terms of terminals and molecular partitions. For example, the grafting of per-6-deoxy-(6-thio)-β-cyclodextrin (terminated with –SH) onto Ag nanoparticles cause LSPR to blueshift and weaken in the absorption amplitude, consistent with our results. On the contrary, the grafting of 3-mercaptopropanoic acid, benzenethiol and 4-pyridinethiol leads to a red shift and absorption amplification of LSPR of Ag nanoparticles.

Why can achiral C8-G weaken the plasmonic CD? Since the chiroptical response inherently originates from the AgNH helicity, the chiroptical weakening could be attributed to the helicity degradation caused by the grafting of C8-G, especially for C8-SH where the possibility that the thiol group (-SH) can etch Ag atoms has been discussed. However, helicity degradation barely occurs for 1RH-AgNHS (Figure 3.9), which excludes its contribution to the observed chiroptical weakening.

The CD of an AgNH array can be evaluated by

\[ CD = \frac{4}{\varepsilon_0 \varepsilon_r} CG'' \]  

where C is the optical chirality of AgNHS, \( G'' \) is the imaginary part of the isotropic mixed electric–magnetic dipole polarizability of AgNHS. \( \varepsilon_0 \) and \( \varepsilon_r \) are the dielectric permittivity of vacuum and the medium surrounding the AgNHS, respectively.

We previously reported that the CD of AgNHS is contributed from radiative loss attributed to that some of light energy entered into the AgNHS are released as re-emitted radiation, and Ohmic loss ascribed to that the rest are absorbed in the AgNHS and eventually become heat. The ratio
of radiative loss to Ohmic loss was calculated to be ~10 for the L-mode.\textsuperscript{[69]} As such, it can be assumed that the grafting of C8-G on the AgNHs has a negligible effect on \( C \) and \( G'' \) of the L-mode, due to the negligible light absorption in the AgNHs. The L-mode CD is reciprocally proportional to \( \varepsilon_r \). Ambient exposure inevitably makes the AgNHs spontaneously covered with a layer of silver oxide (Ag\(_x\)O) with a thickness of ~5 nm (Figure 3.9b). The AgNH arrays with a spiral-to-spiral spacing of ~100 nm are filled with air, and the radiative loss stems from multiple reflections propagating in the air trapped in the porous arrays. As a result, the effective medium surrounding the pristine AgNH arrays without the alkyl grafting is composed of the trapped air and the Ag\(_x\)O layers, that is, \( \varepsilon_r^{air:Ag\_xO} \) determined by the volume fractions of air and Ag\(_x\)O. The grafting of C8-G turns the effective medium to be described by \( \varepsilon_r^{air:m:Ag\_xO} \). Combining Equations (3.1) and (3.2) leads to

\[
\frac{\varepsilon_r^{air:m:Ag\_xO}}{\varepsilon_r^{air:Ag\_xO}} = \frac{1}{1+\Delta CD\%} \quad (3.3)
\]

where \( \lambda_{\text{max},0} \) is at ~560 nm for the L-mode. The calculation in Figure 3.7b shows the medium dielectric ratio of \( \varepsilon_r^{air:m:Ag\_xO} \) to \( \varepsilon_r^{air:Ag\_xO} \) rises with increasing the dielectric permittivity of C8-G (\( \varepsilon_r^m \)), which is 1.04 for C8-H, 1.16 for C8-COOH, 1.26 for C8-NH\(_2\) and 1.35 for C8-SH. The calculation results are discussed. First, \( \varepsilon_r^{air:m:Ag\_xO} \) is determined by not only \( \varepsilon_r^m \) but also the packing density of the C8-G SAMs. Compact packing of molecules with high \( \varepsilon_r^m \) leads to high value of \( \varepsilon_r^{air:m:Ag\_xO} \). C8-H with the smallest \( \varepsilon_r^m \) tends to physically adsorb on the Ag\(_x\)O:AgNHs with random orientation and low packing density, resulting in the slight increase of \( \varepsilon_r \) in 1.04 times. \( \varepsilon_r^m \) and the packing density tend to rise with increasing the contact BE, accounting for the increase of the medium dielectric ratio. Second, the grafting of C8-G tends to etch Ag\(_x\)O, resulting in the replacement of Ag\(_x\)O with the C8-G SAMs. The Ag\(_x\)O etching tends to be exacerbated with increasing \( \varepsilon_r^m \), especially for C8-NH\(_2\) and C8-SH (Figure 3.9b). In the \( \lambda \) range of 300-700 nm, \( \varepsilon_r^{Ag\_xO} < 2.4 \text{[70]} \) which is smaller than \( \varepsilon_r^m \) of C8-NH\(_2\) and C8-SH. Therefore, the replacement of Ag\(_x\)O with C8-NH\(_2\) and C8-SH also leads to the increase of \( \varepsilon_r \). Third, the chiroptical weakening
effect on the plasmonic L-mode is attributed to the increase of $\varepsilon_r$, according to Equation (3.2). With increasing BE of the Ag-G contacts, $\varepsilon_r$ tends to rise and exacerbate the chiroptical weakening.

The ratio of radiative loss to Ohmic loss was evaluated to be $\sim 7$ for the T-mode at $\lambda_{max,0}$ of $\sim 370$ nm, which is smaller than that of the L-mode.\textsuperscript{[69]} It is illuminated that the T-mode has contribution of light absorption in the metal more than the L-mode, and the grafting of C8-G would affect C and G” of the T-mode. Hence, Equation (3.3) could not be used and the $\varepsilon_r$-induced chiroptical weakening would not make a full contribution to lowering the T-mode CD. Considering the fact that the T-mode CD is lowered more seriously than the L-mode CD (Figure 3.7a), the T-mode CD would be quenched by some other factors. One possibility is that the grafted C8-G, especially C8-NH2 and C8-SH, gives rise to partial withdrawal of electron density from the AgNHs towards the alkyl molecules, leading to a decrease of plasmonic chirality (C).\textsuperscript{[71]} High BE of the Ag-G contacts facilitates the electron withdrawal, leading to the exacerbation of the chiroptical weakening. Given that the electron withdrawal is unlikely to be caused by the physical adsorption of C8-H on AgNHs, the physical adsorption-induced $\Delta$CD\% of the T-mode ($-4.9\%$) is roughly equal to that of the L-mode ($-4.1\%$). Additionally, it was recently reported that on the curved surfaces of Au nanoclusters, the grafting of achiral thiolates could create a chiral adsorption pattern via the formation of S-Au-S staple motifs,\textsuperscript{[72, 73]} illustrating that the molecular adsorption on a curved surface could differ remarkably from the SAM on a flat surface, and the thiolate-induced chiral surface patterns could affect the chiroptical activity of AgNHs via the chirality-related coupling. Note that the grafting of C8-SH on the curved surfaces of AgNHs with $d$ of $\sim 45$ nm is unknown at present because of the major limitations of current surface characterization techniques, although no topography change was induced by the grafting of C8-SH as observed by SEM (Figure 3.9a) and TEM images.
Figure 3.9 (a) SEM top-down images and (b) TEM images of the pristine 1RH-AgNH arrays without and with the grafting of C8-G. Inset: (b) the arrows highlight the Ag_xO layers. The grafting of C8-NH_2 and C8-SH appears to cause the etching of Ag_xO.

### 3.2.2 Summary

In summary, a close-packed array of AgNHs generated by GLAD exhibits strong chiroptical activity composed of a plasmonic T-mode at ~370 nm and broadband L-mode centred at ~570 nm, with CD signs opposite to one another. The grafting of C8-G on the AgNHs quenches the two plasmonic CD modes, and the T-mode is weakened more seriously than the L-mode. The CD deterioration is exacerbated with increasing BE of the Ag-G contacts, which is attributed to the increase of $\varepsilon_r$ and the enhancement of electron withdrawal from the AgNHs towards C8-G. This work contributes to devising a simple method to quantitatively study the chiral AgNHs–molecule interactions. This work has been published in *Small* (2016, 12: 6698-6702).[^74]
3.3 Enantioselective weakening CD of AgNHs induced by grafting with enantiomeric glutathione

3.3.1 Results and discussion

Based on an understanding of the interaction between the molecules and AgNHs, we devise a plasmonic CD-assisted method toward exploring the enantiodifferentiation. Enantiomers inherently interact differently with LCP and RCP radiation in terms of optical absorbance (A), resulting in the technique of CD typically utilized to differentiate enantiomers. To decouple CD from enantiomer concentration and optical path length, an anisotropy $g$ factor is evaluated by $^{[75]}$

$$g = \frac{2g_{CD}}{A_{LCP}+A_{RCP}}$$ (3.4)

Glutathione (GSH, with L- and D-configuration) absorbs UV light (Figure 3.10b) and is chiroptically active at wavelength $\lambda < 260$ nm (Figure 3.10a). As well known, molecules with terminals (G: –SH, –NH$_2$ and –COOH) can be grafted onto noble metals (M: Au, Ag) through the formation of M–G contacts (M–S, M–NH$_2$ and M–OOC). M–S has the mostly covalent nature and highest bond energy.$^{[76]}$

Figure 3.10 (a) CD (in black) and anisotropic $g$ factor spectra of 10 µmol/L L-GSH. (b) UV absorption spectra of an aqueous buffered solution (pH of ~3) containing 1 µmol/L L- and D-GSH.
GSH is chemically grafted on silver nanospirals (AgNHs), leading to a weakening of chiroptical activity of an AgNH array in the visible region. The chiroptical weakening sensitively varies with the absolute configuration of GSH, resulting in a differentiation of L- and D-GSH with a AgNH-induced anisotropic $g$ factor of $\sim0.5$ that is independent on the AgNH helicity. The AgNH-induced anisotropy $g$ factor is superior to those obtained by other methods, by 2-4 orders of magnitude. It is the largest achieved up-to-date, as high as one-fourth of the theoretical maximum. The proposed method can be generally adapted to differentiate bio-enantiomers, paving the way to develop a wide range of chirality-related bio-applications.

Figure 3.11 AgNH-induced differentiation of L- and D-GSH, characterized by CD: pristine 1LH-AgNHs (red lines in a, b) and 1RH-AgNHs (blue lines in c, d); AgNHs grafted with L-GSH (orange lines in a, c) and D-GSH (green lines in b, d). The arrows in (a-d) illuminate the GSH induced CD weakening of the plasmonic L-mode (highlighted by green background).
As we known, enantiomers typically have an ellipticity of $10^{-3}$-$10^{-1}$ degree, 2-4 orders of magnitude lower than that of the AgNH array. The AgNH array has extremely high chiroptical response, owing to the wavelength-comparable size, generation of helical displacement current in the continuous NSs, and plasmonic coupling in the closely-packed array. The grafting of GSH on AgNHs barely affects the UV chiroptical mode but quenches the visible mode, regardless of the chirality of GSH and helicity of AgNHs (Figure 3.11). The chiroptical quenching can be quantitatively evaluated by

$$\Delta CD_{max} % = \frac{(CD_{max,e} - CD_{max,0})}{CD_{max,0}} \times 100\%$$ (3.5)

where $CD_{max}$ is the maximum CD value of L-mode. The subscript “e” and “0” represent an AgNH array with and without the grafting of enantiomers, respectively. The interaction index $\Delta CD_{max} %$ is statistically evaluated from multiple (at least 3 times) to obtain an algebraic average value. It is evaluated $\Delta CD_{1L}^{1L:(L)} %$ (the grafting of 1L-AgNHs with L-GSH) to be -27.0% (Figure 3.11a), and $\Delta CD_{max}^{1L:(D)} %$ (the grafting of 1L-AgNHs with D-GSH) to be -15.5% (Figure 3.11b). $\Delta CD_{max} %$ has a negative value owing to the chiroptical quenching effect. The visible chiroptical activity of 1L-AgNHs is quenched by L-GSH more than by D-GSH, resulting in differentiation of L- and D-GSH with a chiroplasmon-induced anisotropy $g$ factor defined as

$$g_{1L:GSH} = 2 \frac{\Delta CD_{max}^{1L:(L)} %}{\Delta CD_{max}^{1L:(D)} %}$$ (3.6)

where $g_{1L:GSH}$ is calculated to be 0.54. On the contrary, L-GSH gives rise to a chiroptical weakening effect on 1R-AgNHs smaller than D-GSH, with $\Delta CD_{max}^{1R:(L)} %$ of -12.5% (Figure 3.11c) and $\Delta CD_{max}^{1R:(D)} %$ of -21.0% (Figure 3.11d). $g_{1R:GSH}$ is calculated to be 0.51 roughly equal to $g_{1L:GSH}$, illustrating that AgNHs can differentiate L- and D-GSH with an anisotropy $g$ factor of $\sim$0.5 independent on the plasmonic helicity. The chiroplasmon-induced differentiation of GSH is summarized in Figure 3.12.
Figure 3.12 In spite of different definitions of the anisotropy g factor (eqn. 1 versus eqn. 4), they are compatible to evaluate the differentiation of single enantiomer from its mirror image. According to eqn. 1, the anisotropy g factor of GSH (10 μmol/L, in an aqueous buffered solution with pH of ~3) is ~10^{-4}; it was reported that conjugation of GSH with achiral semiconductor quantum dots\cite{77} and plasmonic nanoclusters\cite{78,79} gives rise to an anisotropy g factor of ~10^{-5} and 10^{-4}-10^{-3}, respectively. Remarkably, the chiroplasmon-induced anisotropy g factor is larger than those obtained by the above-mentioned methods by 2-4 orders of magnitude. Analogous to eqn. 1, it is derived from eqn. 4 that the chiroplasmon-induced anisotropy g factor has the theoretical maximum of 2, given that the interaction index $\Delta\mathcal{C}_C^\text{max}$ has a sign the same as $\Delta\mathcal{C}_D^\text{max}$ due to the chiroptical quenching effect. The chiroplasmon-induced g factor is one-fourth of the theoretical maximum, the highest achieved up-to-date.

The L-GSH causes more chiroptical weakening effect on 1L-AgNHs than D-GSH does, and D-GSH causes more chiroptical weakening effect on 1R-AgNHs than L-GSH does (Figure 3.12). The symmetric quenching effect closely relates to the chiroplasmon-enantiomer interaction, which is under study recently.
3.3.2 Summary

In summary, I report on utilizing chiroptically active AgNH arrays to dramatically enhance the differentiation of L-GSH and D-GSH. The chiroplasmon-enhanced anisotropy $g$ factor of GSH is superior to those obtained by other methods by 2-4 orders of magnitude, and is the largest achieved up-to-date as high as one-fourth of the theoretical maximum. The AgNH arrays have such extremely strong chiroptical activity that significantly amplifies the chiroplasmon-enantiomer interaction, accounting for the dramatic enhancement of enantiomer differentiation.

The homochirality leads to the chirality-dependent interaction of biological systems and chiral drugs/pesticides. Given a quick development of drug carriers based on the plasmonic nanoparticles, this work provides an additional degree of freedom in terms of chiroptical activity to study the biological functions of chiral drugs and pesticides, paving the way to develop a wide range of chirality-related applications in the areas of pharmaceutical and agricultural production, food quality control, disease diagnosis and treatment, and environmental protection.
4 Helical Nanoparticle-Induced Enantioselective Amplification of Molecular Optical Activity

4.1 Introduction

Enantiodifferentiation can be enhanced by grafting bio-enantiomers on chiral metamaterials, such as Au gammadions,\textsuperscript{[14]} shuriken nanostructure,\textsuperscript{[27]} and Ag nanohelices\textsuperscript{[80]} that have structural helicity and strong plasmonic optical activity.\textsuperscript{[55, 81]} Due to the sensitive change in plasmonic optical activity of chiral metamaterials with altering dielectric constant of the medium,\textsuperscript{[74]} the bio-enantiomer grafting gives rise to the chirality-dependent change in the plasmonic optical activity and leads to the enhanced enantiodifferentiation. Most of Biomolecules typically absorb UV light with a wavelength ($\lambda$) shorter than 250 nm. A question is intuitively raised about the possibility to directly amplify the optical activity of enantiomers that are immobilized on chiral metamaterials, which is lack of investigation to the best of our knowledge. The hypothesis is demonstrated, for the first time, in this work. Enantiomeric optical activity, characterized by CD spectroscopy, can be enantioselectively amplified by covalently grafting enantiomers on silver nanohelices generated by glancing angle deposition (GLAD).	extsuperscript{[82]} Clockwise/counterclockwise substrate rotation leads to sculpturing nanohelices in the right/left-handed, and helical pitch ($P$) can be facilely controlled by engineering substrate rotation rate (refer to chapter 2). Such the flexible engineering of the metallic helicity paves the way to tailoring the optical activity enhancement as a function of $P$ and helical handedness.

4.2 Result and Discussion

Amplification of molecular OA is investigated in ($R$)- and ($S$)-1,1’-Binaphthyl benzo-27-crown-8 benzyl (1, 2-dithiolan-3-yl) pentanoate (i.e., ($R$)-1 and ($S$)-1, Figure 4.1a, b) terminated with “S-S” bonds. Grafting of enantiomers 1 on noble metals (e.g., Ag) causes the S-S bonds to be spontaneously cleaved to create two Ag-S contacts. Enantiomers 1 have strong light absorption at a wavelength shorter than 250 nm and weak UV absorption at 250 – 350 nm (Figure 4.1c-I). Resonantly, enantiomers 1 exhibit strong bisignate CD peaks located at 227 and 240 nm and weak,
broad monosignate CD peaks located at 250 – 350 nm, which flip around the zero-CD axis while switching the enantiomeric chirality (Figure 4.1c-II).

Figure 4.1 Characterization of optical activity (OA) of enantiomers (R)-1 and (S)-1: (c) dispersed in ethanol:CH₂Cl₂ (9:1, volume ratio) with a concentration of 0.03 mmol/L, and (d) grafted on right-handed (RH) AgHNPs with a helical pitch (P) of ~4.5 nm. Molecular structure: (a) (R)-1, (b) (S)-1. UV-visible spectra: (c-I) absorption, (d-I) extinction (i.e., Ext), (II) CD, and (III) anisotropic g-factor. (c) (R)-1 (blue lines), and (S)-1 (red lines). (d) Pristine RH-AgHNPs (black lines), and the RH-AgHNPs grafted with (R)-1 (blue lines). (d-I) Subtraction of the black spectrum from the blue spectrum, in a wavelength range of 220 – 340 nm, results in the orange spectrum. Division of the blue spectrum in (d-II) by the orange spectrum in (d-I), in a wavelength range of 220 – 300 nm, gives rise to the orange spectrum shown in (d-III)
according to eq. 4.1. Insets: SEM cross-sectional image of (d-II) the pristine RH-AgHNPs and (d-III) the RH-AgHNPs modified with (R)-1 (scale bar: 100 nm). The arrows in (d-II) and (d-III) represent red shift of the transverse plasmonic mode of the RH-AgHNPs due to the enantiomeric grafting.

To quantitatively evaluate the optical activity amplification, anisotropic g-factor was calculated to evaluate the optical activity per enantiomer, according to

\[
g = \frac{\text{CD}}{16500A} \quad (4.1)
\]

where CD is the ellipticity (units: millidegree, or mdeg), and A represents the absorptance for enantiomers dissolved in solution or the extinction (i.e., Ext) for the solid samples. Enantiomers 1 have an OA as strong as \(3\times10^{-3}\) at \(\sim240\) nm (Figure 4.1c-III).

To facilely study the optical activity amplification of enantiomers 1 covalently grafted on metallic nanohelices, it is a prerequisite that metallic nanohelices should have negligible optical activity in the deep-UV region (at the wavelength shorter than 300 nm) where the enantiomeric optical activity occurs. Metallic nanohelices typically have \(P > d\) (wire diameter), and exhibit multiple CD peaks in the UV-visible region.\(^{[81]}\) For instance, silver nanohelices with a \(P > 150\) nm exhibit optical activity composed of the longitudinal plasmonic mode in the visible region,\(^{[83]}\) the transverse plasmonic mode at the wavelength of \(\sim370\) nm, and the dielectric mode in the deep-UV region\(^{[84]}\) owing to strong Ohmic loss (Figures 4.2a,b).\(^{[68]}\)
The deep-UV optical activity has an ellipticity as high as ~2 degree, which is markedly larger than that of enantiomers 1 in roughly two orders of magnitude. The enantiomeric optical activity would be seriously screened by the chiroplasmonic optical activity, resulting in an impossibility to study the chiroptical enhancement of the grafted enantiomers. In our previous report, GLAD with fast substrate rotation was employed to make $P < d$ (i.e., $P < \sim 70$ nm under the given GLAD conditions), and silver nanohelices appear to be achiral nanoparticles with hidden helicity (i.e., silver helical nanoparticles, or AgHNPs).[84] The AgHNPs with a $P$ in a range of 2.5 – 40 nm, which appear to have $P$-independent achiral NP-profile (Figure 4.3).
Stemming from the hidden helicity, the AgHNPs exhibit an intrinsic optical activity that is composed of the longitudinal plasmonic mode in the visible region and the transverse plasmonic mode at ~370 nm, and is negligible in the deep-UV region (Figure 4.4). When HNPs are made from Au (e.g., AuHNPs), AuHNPs with a nominal $P$ of ~5 nm (inset in Figure 4.2c) exhibit LSPR and resonant bisignate CD at the wavelength longer than 450 nm, and non-negligible dielectric CD in the deep-UV region (Figures 4.2c, d). As a result, the AgHNPs were selected to study the chiroptical enhancement of the grafted enantiomers.
When $(R)$-1 is covalently grafted onto the right-handed AgHNPs (i.e., RH-AgHNPs) with a $P$ of ~4.5 nm, the transverse CD mode of the RH-AgHNPs has an evident red shift (marked by red arrows in Figures 4.1d-II and 4.1d-III), due to the enantiomer-induced increase of dielectric constant of the medium for the AgHNPs.[74] More importantly, the enantiomer-grafted RH-AgHNP array exhibits an extinction peak at ~240 nm (blue spectrum, Figure 4.1d-I) and the bisignate CD peaks at 231 and 246 nm, which are the chiroptical characteristics of the grafted enantiomers $(R)$-1. Given that the extinction of the enantiomer-grafted RH-AgHNP array is contributed from that of the AgHNPs and the grafted enantiomers, subtraction of the extinction spectrum of the pristine array (black spectrum, Figure 4.1d-I) from that of the enantiomer-grafted array (blue spectrum, Figure 4.1d-I) gives rise to the absorption of the grafted enantiomers (orange spectrum, Figure 4.1d-I) from that of the enantiomer-grafted array (blue spectrum, Figure 4.1d-I) gives rise to the absorption of the grafted enantiomers (orange spectrum, Figure
4.1d-I), which was used to calculate the anisotropic g-factor of the immobilized (\textit{R})-1 (orange spectrum, Figure 4.1d-III) according to eq. 4.1. The comparison of the grafted and dispersed enantiomers in terms of anisotropic g-factor (orange spectrum in Figure 4.1d-III versus blue spectrum in Figure 4.1c-III) was made to quantitatively study the grafting-induced amplification of the enantiomeric optical activity, through calculating an enhancement factor (\textit{EF}) given by,

\[ EF = \frac{A_{ad}}{A_{sol}} \quad (4.2) \]

where \( A_{sol} \) and \( A_{ad} \) represents the integrated area of the bisignate g-factor peaks of the enantiomers dispersed in the solvent and grafted on the AgHNPs, respectively, in the deep-UV region.

\textit{EF} of enantiomers 1 immobilized on the AgHNPs with a \( P \) of \(~3 \text{ nm} \) was evaluated as a function of the enantiomeric and helical handedness. The surface immobilization makes the bisignate CD peaks of the grafted enantiomers 1 markedly redshift compared to that of the dispersed enantiomers (red and blue spectra versus green spectrum, Figures 4.5a and 4.5d). The grafting of (\textit{R})-1 on the RH- and LH-AgHNPs gives rise to an \textit{EF} value of 4.6 ± 1.9 and 1.2 ± 0.3, respectively; the immobilization of (\textit{S})-1 on the RH- and LH-AgHNPs causes an \textit{EF} value of 2.1 ± 0.9 and 4.3 ± 0.4, respectively. It is illustrated that the grafting of enantiomers 1 on the AgHNPs with the sub-5 nm \( P \) leads to an enantioselective amplification of the enantiomeric OA: the RH-AgHNPs tend to cause stronger optical activity amplification for (\textit{R})-1 than the LH-AgHNPs, and vice versa for (\textit{S})-1. The RH-AgHNPs with the sub-5 nm \( P \) provides the maximum \textit{EF} of 7.4 for (\textit{R})-1, and the LH-AgHNPs causes that of 4.7 for (\textit{S})-1 (marked by asterisks, Figures 4.5c and 4.5f). Intriguingly, when \( P \) is elongated to \(~10 \text{ nm} \), the enantioselective optical activity amplification tends to disappear: (\textit{R})-1 has an \textit{EF} value of 1.0 ± 0.2 and 1.5 ± 0.4 on the RH- and LH-AgHNPs, respectively (Figure 4.5b); (\textit{S})-1 has an \textit{EF} value of 1.8 ± 0.4 and 1.1 ± 0.1 on the RH and LH-AgHNPs, respectively (Figure 4.5e).
Figure 4.5 AgHNP-induced amplification of the OA of enantiomers (a-c) (R)-1 and (d-f) (S)-1 that are anchored on left handed (LH, in red) and RH (in blue) AgHNPs as a function of $P$ in a range of 2.5 – 40 nm, e.g. (a, d) $P$ of ~3 nm and (b, e) $P$ of ~10 nm. Amplification of the enantiomeric OA is quantitatively characterized by anisotropic $g$-factor spectra using the method described in Figure 4.1d. The enantiomers 1 are grafted on achiral AgNPs (black solid lines in (a, d), and black dash lines in (c, f)), and are dispersed in ethanol:CH$_2$Cl$_2$ (9:1, volume ratio) with a concentration of 0.03 mmol/L (green solid lines in (a, b, d, e), and green dash lines in (c, d)). (b) The bisignate $g$-factor peaks in the deep-UV region are characterized by spectral parameters of $\lambda_{\text{max},1}$, $g_{\text{max},1}$, $\lambda_{0,1}$, $\lambda_{\text{max},2}$, $g_{\text{max},2}$ and $\lambda_{0,2}$. (c, d) Plots of enhancement factor ($EF$) as a function of $P$. According to eq. 2, $EF$ of the enantiomers dispersed in the solvent is equal to 1, represented by the green dash lines. The blue asterisk in (c) represents the maximum $EF$ of 7.4 for (R)-1 grafted on the RH-AgHNPs with a $P$ of 2.9 nm, and the red asterisk in (f) represents the maximum $EF$ of 4.7 for (S)-1 grafted on the LH-AgHNPs with a $P$ of 2.4 nm.
To systematically study the dependence of the optical activity amplification on the AgHNP helicity, $EF$ was evaluated as a function of the helical handedness and $P$ in a range of 2.5 – 40 nm (Figures 4.7 and 4.8). It should be noted that the anchoring of enantiomers 1 has a negligible effect on the helical structures of the AgHNP (inset in Figure 4.1d-III versus inset in Figure 4.1d-II), and the optical activity amplification of the grafted enantiomers could not contribute from the solvent effect (Figure 4.6).

For $<R>-1$, the grafting on the LH-AgHNP leads to an $EF$ value slightly varying in a range of 1.2 – 1.8 on average, nearly independent on $P$ (red symbols, Figure 4.5c); and the attachment to
the RH-AgHNPs with a sub-5 nm $P$ causes a 4.7-fold amplification on average, which tends to vanish at $P > 5$ nm (blue symbols, Figure 4.5c). The grafting of (S)-1 results in an opposite helicity-related dependence: the immobilization on the RH-AgHNPs causes a $P$-independent $EF$ value varying in a range of 1.5 – 2 on average (blue symbols, Figure 4.5d); that on the LH-AgHNPs with the sub-5 nm $P$ has an average $EF > ~3$, and the optical activity amplification tends to disappear at $P > 5$ nm (red symbols, Figure 4.5f). The helicity-dependent variation of the $EF$ values is coincident with that of the characteristic parameters of CD spectra (inset in Figure 4.5b) including $g_{\text{max},1}$, $g_{\text{max},2}$ and $\lambda_{0,2}$ (Figure 4.9), although the wavelength-related spectral parameters (including $\lambda_{\text{max},1}$, $\lambda_{0,1}$ and $\lambda_{\text{max},2}$) appear not to markedly vary with the helicity (Figure 4.10). It is illuminated that the chiroptical amplification (in terms of $g_{\text{max},1}$ and $g_{\text{max},2}$) and the spectral broadening (i.e., the red shift of $\lambda_{0,2}$) account for the evident optical activity amplification at the sub-5 nm $P$.

Figure 4.7 Anisotropic $g$-factor (solid lines) and extinction (i.e., Ext, dash lines) spectra of enantiomers ($R$)-1 grafted on LH-AgHNPs (red lines) and RH-AgHNPs (blue lines), with a nominal $P$ of (a) ~2.5 nm, (b) ~4.5 nm, (c) ~6 nm, (d) ~10 nm, (e) ~19 nm, (f) ~28 nm, and (g) ~38 nm. Extinction and anisotropic $g$-factor spectra were calculated by the method described in Figure 4.1d.
Figure 4.8 Anisotropic $g$-factor (solid lines) and extinction (i.e., Ext, dash lines) of enantiomers (S)-1 grafted on LH-AgHNPs (red lines) and RH-AgHNPs (blue lines), with a nominal $P$ of (a) ~2.5 nm, (b) ~4.5 nm, (c) ~6 nm, (d) ~10 nm, (e) ~19 nm, (f) ~28 nm, and (g) ~38 nm. Extinction and anisotropic $g$-factor spectra were calculated by the method described in Figure 4.1d.
Figure 4.9 Summary of the spectral parameters of the deep-UV bisignate g-factor peaks shown in Figures 4.7 and 4.8, as a function of $P$: (a) $(R)$-1, (b) $(S)$-1; (I) $g_{\text{max},1}$, (II) $g_{\text{max},2}$, and (III) $\lambda_{0,2}$. Green dash lines: enantiomers 1 dispersed in ethanol:CH$_2$Cl$_2$ (9:1, volume ratio) with a concentration of 0.03 mmol/L; black dash lines: enantiomers 1 grafted on the achiral AgNPs.
Figure 4.10 Summary of the spectral parameters of the deep-UV bisignate g-factor peaks shown in Figures 4.7 and 4.8, as a function of $P$: (a) ($R$)-1, (b) ($S$)-1; (I) $\lambda_{\text{max},1}$, (II) $\lambda_{0,1}$, and (III) $\lambda_{\text{max},2}$.

Green dash lines: enantiomers 1 dispersed in ethanol:CH$_2$Cl$_2$ (9:1, volume ratio) with a concentration of 0.03 mmol/L; black dash lines: enantiomers 1 grafted on the achiral AgNPs.

When enantiomers ($R$)-1 and ($S$)-1 are attached to achiral AgNPs (black spectrum, Figures 4.5a and 6.5d), although the enantiomeric optical activity appears to have a red shift compared to that of the dispersed enantiomers, the $EF$ values were evaluated to be 1.2 and 1.3, respectively (black dash line, Figures 4.5c and 4.5f). The slight chiroptical enhancement may be ascribed to the molecular assembly at the achiral surfaces. The $EF$ values on the achiral AgNPs are evidently smaller than those of ($R$)-1 on the RH-AgHNPs and those of ($S$)-1 on the LH-AgHNPs at the sub-5 nm $P$. It is indicated that such the chiroptical enhancement is attributed to not only the surface
grafting-induced aggregation but also the helical topography-induced change of enantiomeric absolute configuration, and the latter makes more significant contribution.

Figure 4.11 AgHNP-induced amplification of the OA of enantiomers 2 grafted on LH- (red lines) and RH-AgHNPs (blue lines) with a $P$ of $\sim 4.5$ nm and on achiral AgNPs (in black), characterized by anisotropic $g$-factor spectra: (a) $(R)$-2, (b) $(S)$-2. Green spectra in (a, b) represent enantiomers 2 dispersed in ethanol:CH$_2$Cl$_2$ (9:1, volume ratio) with a concentration of 5 μmol/L. Insets: molecular structure of (a) $(R)$-2 and (b) $(S)$-2. (c) $EF$ values of enantiomers 2 grafted on LH-AgHNPs (red columns), RH-AgHNPs (blue columns), and achiral AgNPs (black columns). The blue asterisk represents the maximum $EF$ value of 8.2 for $(R)$-2 immobilized on the RH-AgHNPs, and the red asterisk represents the maximum $EF$ value of 8.9 for $(S)$-2 grafted on the LH-AgHNPs.

The bisignate CD peaks of enantiomers 1 are assigned to the bi-naphthalic chromophores; to simplify the study in the mechanism of the OA amplification, enantiomers 1,1’-Binaphthyl-2,2’-dithiol (enantiomer 2, inset in Figures 4.11a, b) were synthesized and grafted on the LH- and RH-AgHNPs with a sub-5 nm $P$ of $\sim 4.5$ nm through the formation of two Ag-S contacts. Dispersed enantiomers 2 exhibit the bisignate CD peaks at the wavelength of 220 – 280 nm, and the peak at the wavelength of $\sim 235$ nm (the left-bisignate peak) is weaker than that at $\sim 255$ nm (the right-bisignate peak). When $(R)$-2 are immobilized on the RH-AgHNPs and $(S)$-2 are grafted on the LH-AgHNPs, the left-bisignate $g$-factor peak cannot be fully monitored (orange spectra, Figures 4.12a-III and 4.12c), so that the optical activity amplification of enantiomers 2 is evaluated in terms of
the right-bisignate g-factor peak. Compared to the optical activity of the dispersed 2 (green spectrum, Figures 4.11a, b), the grafting of (R)-2 on the RH- and LH-AgHNPs with the sub-5 nm P leads to an $EF$ value of 8.6 ± 3.3 and 5.3 ± 1.3, respectively; and the immobilization of (S)-2 on the RH- and LH-AgHNPs leads to an $EF$ value of 1.8 ± 0.3 and 5.0 ± 3.6, respectively (Figure 4.11c). The grafting of (R)-2 on the RH-AgHNPs leads to the maximum 13.1-fold amplification, and that of (S)-2 on the LH-AgHNPs gives rise to the maximum 8.9-fold enhancement (marked by the asterisks in Figure 4.11c). The RH- and LH-AgHNPs with the sub-5 nm P give rise to the enantioselective amplification of the enantiomeric OA of (R)-2 and (S)-2, respectively, coincident with that of enantiomers 1. The OA amplification obtained in this work is comparable to the 11-fold amplification achieved by enhancing the optical chirality through creating the standing wave.\textsuperscript{12} However, it should be noted that plasmonic CD are not excited in the deep-UV region given the transverse plasmonic mode of the AgHNPs at ~370 nm; hence, the optical activity amplification should not be ascribed to the plasmonic effect on amplifying the optical chirality of near-field scattering that is accessible for the grafted enantiomers.
Figure 4.12 UV-Visible spectra: (a-I) Ext, (a-II) CD, (a-III) anisotropic g-factor. (a) Pristine RH-AgHNPs (black lines), and the RH-AgHNPs grafted with (R)-2 (blue lines). (a-I) Subtraction of the black spectrum from the blue spectrum, in a wavelength range of 200 – 320 nm, results in the orange spectrum. Division of the blue spectrum in (a-II) by the orange spectrum in (a-I), in a wavelength range of 200 – 320 nm, gives rise to the orange spectrum shown in (a-III) according to eq. 4.1. Anisotropic g-factor spectra of (b) LH-AgHNPs grafted with (R)-2, (c) LH-AgHNPs grafted with (S)-2, (d) RH-AgHNPs grafted with (S)-2 as shown in range of 200-300 nm. Inset: (b) SEM cross-sectional image of the pristine LH-AgHNPs and (d-III) grafted (R)-2 LH-AgHNPs (scale bar: 100 nm).

The grafting of (R)-2 and (S)-2 on the achiral AgNPs (black spectra, Figures 4.10a-b) causes an $EF$ value of $4.9 \pm 1.3$ and $2.9 \pm 0.6$, respectively, which are markedly smaller than those of the AgHNP-induced enantioselective amplification. It should be noted that the optical activity amplification of enantiomers 2 grafted on the AgHNPs and achiral AgHPs is generally larger than
that of enantiomers 1 (Figure 4.11c versus Figures 4.5c and f). The bi-naphthalic chromophore of enantiomers 2 are directly bound with the metallic surfaces but that of enantiomers 1 aren’t, indicating that the absolute configuration of the bi-naphthalic chromophore immobilized at the surfaces plays an essential role in the optical activity amplification.
5 Water Effect on CD of AgNHs and AgHNPs

5.1 Introduction

In the previous chapters, I fully discussed the interaction of molecules and Ag helical nanoparticles. As we know, AgNH arrays with high array porosity shows strong chiroptical activity composed of a plasmonic T-mode at \( \sim 370 \) nm and broadband L-mode centred at \( \sim 570 \) nm, with CD signs opposite to one another. Because of the limitation of nano-fabrication techniques, it is difficult to minimize wire diameter \((d)\) and consequently helical pitch \((P)\) to the sub-10-nm molecule-comparable scale that prevent the study of plasmonic CD at dimensions approaching the physical limit. However, when operating GLAD with a high speed of substrate rotation, that silver nanoparticles (AgHNPs) have intrinsic hidden helicity were generated and the helical pitch is nominally smaller than wire diameter. The CD spectra of AgHNPs are composed of the plasmonic peak at \( \sim 370 \) nm, a peak at \( \sim 340 \) nm, and bisignated peaks with very weak intensity in the visible region. The \( \sim 340\)nm CD peak is assigned to the shoulder plasmonic mode, as there is a shoulder extinction peak at \( \sim 340\)nm.

Considering potential utilization of plasmonic CD in important bioapplications that are typically operated in aqueous solutions, so that it is necessary to study stability of chiroptical activity of chiral nanostructure in the aqueous solutions. I found that immersing AHgNP arrays in water causes the plasmonic mode to redshift and rise in CD amplitude, i.e., a water effect on chiroptical activity. Hydrophilic AgHNP arrays with low array porosity show a reversible water effect, but hydrophobic Ag nanospiral arrays with \( P > d \) and high array porosity have an irreversible water effect.

This chapter quantitatively study the effect of aqueous solvent (or water) on the chiroptical activity of AgHNPs is investigated and compared with that of AgNHs, paving the way to study plasmonic CD approaching the physical limit and exploit chirality-related bioapplications typically operated in aqueous solutions to tackle significant health and environmental problems.
5.2 Results and Discussion

Chiral nanostructure hold promise for chirality-related bioapplications typically operated in aqueous solutions, so that it is fundamentally necessary to study the effect of water on the optical activity of chiral nanostructure. After removal of surface oxides/contaminants using 5% HF, the RH-AgHNPs-$P$ arrays ($P$: 3–70 nm) are hydrophilic, with water contact angles ($\theta$) < 90°; but the RH-AgNHs-215 array is hydrophobic, with a $\theta$ of 120° (Figure 5.1).

![Figure 5.1 Plot of water contact angle ($\theta$) versus $P$. The HF-treated RH-AgHNPs with $P$ less than 70 nm have $\theta$ < 90°, highlighted with a pink background. Insets: photographs of water droplet applied to the surface of RH-AgHNPs-17 (with nominal $P$ of 17 nm, top left) and RH-AgNHs-215 (with $P$ of 215 nm, down right); cross-sectional SEM image of RH-AgNHs-215 deposited on Si wafer; schematic diagrams of RH-AgHNP and RH-AgNH.](image)

This result illustrates that the HF treatment causes AgHNPs to have higher surface energy than AgNHs. Immersing the hydrophilic RH-AgHNPs-17 array in water not only causes the plasmonic extinction and CD peaks to concurrently redshift by roughly 40 nm but also amplifies them, that is, the chiroptical water effect (Figure 5.2a).
Figure 5.2 Chiroptical water effect of (a) RH-AgHNPs-17 and (b) RH-AgNHs-215, characterized by CD and extinction spectroscopies. Blue spectra: pristine arrays in air; red spectra: the arrays immersed in water; green spectra: the water-treated arrays fully dried with N₂. The spectra are vertically shifted for clear comparison. Horizontal black dash lines: zero-CD axis for each CD spectrum. (b) Black and grey arrows mark the transverse (T) and longitudinal (L) plasmonic modes, respectively.

The subsequent drying process makes the extinction and CD return to the original level, showing a reversible water effect that can be further confirmed by the multiple alternating wetting/drying processes (Figures 5.3 and 5.4).
Figure 5.3 Reversible water effect of the plasmonic mode of LH/RH-AgHNPs-17: (a) $\lambda_{\text{Ext, max}}$; (b) $\lambda_{\text{CD, max}}$; (c) $CD_{\text{max}}$; (d) $\Delta\lambda_{\text{Ext, max}}$; (e) $\Delta\lambda_{\text{CD, max}}$; (f) $\Delta CD_{\text{max, %}}$ versus $m$ (the time of alternating wetting/drying processes). (a–c) LH-AgHNPs-17: red arrows represent the wetting processes, and black arrows the drying processes; blue diamonds represent data for the pristine array measured in air ($m = 0$). (d–f): the wetting and drying processes are highlighted with pink and grey backgrounds, respectively; red and blue data represent LH- and RH-AgHNPs-17, respectively; from the first eight ($m$ of 1–8) alternating wetting/drying processes, the water effect indices are statistically evaluated to have an algebraic average value, standard deviation (following the symbol “±”), and the ratio of standard deviation to average value (denoted as the irreversibility, following standard deviation).
Figure 5.4 Reversible water effect of the plasmonic mode of RH-AgHNPs-17: (a) $\lambda_{\text{Ext,max}}$; (b) $\lambda_{\text{CD,max}}$; (c) $CD_{\text{max}}$ versus $m$.

The wetting process can be quantitatively evaluated by

$$\Delta \lambda_{\text{Ext,max}} = (\lambda_{\text{max,water,m}} - \lambda_{\text{max,air,m-1}}) |_{\text{Ext}} \; (5.3a)$$

$$\Delta \lambda_{\text{CD,max}} = (\lambda_{\text{max,water,m}} - \lambda_{\text{max,air,m-1}}) |_{\text{CD}} \; (5.3b)$$
\[ \Delta CD_{\text{max}}\% = \left( \frac{CD_{\text{max,water,m}} - CD_{\text{max,air,m-1}}}{CD_{\text{max,air,m=0}}} \right) \times 100\% \quad (5.4) \]

where the subscript “Ext” represents extinction, “water” the medium of water, “air” the medium of air, and “m” the number of alternating wetting/drying processes. The drying processes can be quantitatively characterized by

\[ \Delta \lambda_{\text{Ext,max}} = (\lambda_{\text{max,air,m}} - \lambda_{\text{max,water,m}})_{\text{Ext}} \quad (5.5a) \]

\[ \Delta \lambda_{\text{CD,max}} = (\lambda_{\text{max,air,m}} - \lambda_{\text{max,water,m}})_{\text{CD}} \quad (5.5b) \]

\[ \Delta CD_{\text{max}}\% = \left( \frac{CD_{\text{max,air,m}} - CD_{\text{max,water,m}}}{CD_{\text{max,air,m=0}}} \right) \times 100\% \quad (5.6) \]

The multiple alternating wetting/drying processes consistently cause the plasmonic extinction and CD peaks to have concurrent red/blue shifts (\( \Delta \lambda_{\text{Ext,max}} \approx \Delta \lambda_{\text{CD,max}} \), Figure 5.3a versus b), and lead to an amplification/reduction of the plasmonic CD (Figure 5.3c). For the LH-AgHNPs-17 array, the first eight (m: 0–8) alternating wetting and drying processes lead to \( \Delta \lambda_{\text{Ext,max}} \) of 41 ± 2 nm and (−41) ± 2 nm (Figure 5.3d), \( \Delta \lambda_{\text{CD,max}} \) of 37 ± 1 nm and (−36) ± 1 nm (Figure 5.3e), and \( \Delta CD_{\text{max}}\% \) of 150 ± 3 % and (−152) ± 4 % (Figure 5.3f), respectively. All the indices of the water effect have ratios of standard deviation to algebraic average value (denoted as the irreversibility) of not more than 5%, and the wetting indices are symmetric around the zero-value axis with the drying ones. This leads to the conclusion that the LH-AgHNPs-17 array has an excellent reversible water effect on chiroptical activity, which can also be seen with the RH-AgHNPs-17 arrays (Figures 5.3d–f and 5.4). The hidden chirality of AgHNPs has little effect on the wetting/drying indices. It has been reported that LSPR of Ag nanospheroids with the aspect ratio of 1 has a red shift of roughly 40 nm when they are immersed in water/glycerol with a refractive index of 1.3,\[^{85}\] in good agreement with our result. Furthermore, LSPR of LH-AgHNPs-17 redshifts linearly with increasing refractive index of the surrounding medium, consistent with the theoretical prediction (Figure 5.5).\[^{86, 87}\]
Figure 5.5 Plot of $\Delta \lambda_{\text{Ext, max}}$ of the LH-AgHNPs-17 array versus refractive index $n$ of the medium (from right top to left down): toluene, dichloromethane, hexane, acetone, ethanol, water, and air.

The LSPR spectral shift ($\Delta \lambda_{\text{Ext, max}}$) can be described as:

$$
\Delta \lambda_{\text{Ext, max}} = m' \left( 1 - e^{-\frac{2T}{l_d}} \right) (n - n_{\text{air}}) = -m' \left( 1 - e^{-\frac{2T}{l_d}} \right) + m' \left( 1 - e^{-\frac{2T}{l_d}} \right) n \quad (5.7)
$$

where $m'$ is the sensitivity factor (in nm per refractive index unit, or nm/RIU), $n$ is the refractive index of the medium, $n_{\text{air}}$ is the refraction index of air (equal to 1 RIU), $T$ is the effective thickness of silver oxides on AgHNPs, and $l_d$ is the electromagnetic field decay length. Equation (5.7) shows that the interception has an absolute value equal to the slope, but the sign opposite to the slope. Evaluated from the linear fitting of Figure 5.5, the intercept is $(-142.7) \pm 13.8$ nm and the slope is $140.2 \pm 10.3$ nm/RIU, in good agreement with Equation (5.7).

The water effect of AgHNPs was compared with that of AgNHS. The RH-AgNHS-215 array with a $P$ of 215 nm has transverse (T) LSPR at a wavelength of roughly 370 nm and longitudinal (L) LSPR at roughly 520 nm (Figures 5.2b and 5.6).
The LSPR of AgNHs is composed of the transverse (T) mode at a wavelength of ~365 nm and longitudinal (L) mode in the visible region (Figure 5.6a). The L mode redshifts with increasing aspect ratio \( l/d \), where \( d \) is the wire diameter and \( l \) is the helical length, given by

\[
l = d + \sqrt{(n\pi(D-d))^2 + (nP-d)^2}
\]

However, the T mode shifts only slightly with the aspect ratio. RH-AgNHs-145 with a \( P \) of 145 nm have an aspect ratio of 4.6, and RH-AgNHs-215 with a \( P \) of 215 nm have an aspect ratio of 5.6. Both in the extinction and CD spectra, the increase in the aspect ratio from 4.6 to 5.6 causes the L mode to redshift from the wavelength of 422 to 518 nm but has little effect on the T mode (Figure 5.6a and b). At \( T_{sub} \) of \(-170 \, ^\circ\text{C}\), Fischer et al. fabricated the array of copper NHs with \( P \) varying from 20 to 100 nm and reported that the plasmonic CD in the visible region redshifts with increasing \( P \), consistent with our results of the redshift of the L mode.

Correspondingly, the AgNH array has a T-plasmonic CD peak at 375 nm with a negative sign and a broad L-plasmonic CD peak centered at ~540 nm with a positive sign. Analogous to the chiroptical water effect of AgHNPs, the wetting/drying process leads to the red/blue shift of the extinction and CD spectra and CD amplification/weakening of the T- and L-plasmonic modes. In terms of \( \Delta \lambda_{\text{Ext, max}} \) and \( \Delta \lambda_{\text{CD, max}} \) of the T- and L-plasmonic modes, the first eight alternating
wetting/drying processes provide the irreversibility of less than 10% and causes $\Delta \lambda_{\text{Ext, max}}$ and $\Delta \lambda_{\text{CD, max}}$ to switch symmetrically around the zero-axis (Figures 5.7a, b, d, e and 5.8a, c).

Figure 5.7 Irreversible water effect on the transverse plasmonic mode of RH-AgNHs-215: (a) $\lambda_{\text{Ext, max}}$; (b) $\lambda_{\text{CD, max}}$; (c) $CD_{\text{max}}$; (d) $\Delta \lambda_{\text{Ext, max}}$; (e) $\Delta \lambda_{\text{CD, max}}$; (f) $\Delta CD_{\text{max}}\%$ versus $m$. Refer to the caption of Figure 7.
This illustrates that the chiroptical activity of AgNHs has a reversible water effect with respect to the resonance wavelength, although the reversibility is less than that of AgHNPs. However, the water effect of AgNHs markedly differs from that of AgHNPs. First, AgHNPs have $\Delta \lambda_{\text{Ext, max}} \approx \Delta \lambda_{\text{CD, max}}$ (Figure 5.3d versus e), indicating that the water effect causes an in-phase extinction-CD shift. However, AgNHs have $\Delta \lambda_{\text{Ext, max}} < \Delta \lambda_{\text{CD, max}}$ (Figure 5.7d versus e), that is, an out-of-phase shift where the CD shifts more than the extinction. Second, for LSPR at ~370 nm, $\Delta \lambda_{\text{Ext, max}}$ of AgHNPs is larger than that of AgNHs (Figure 5.3d versus 5.7d), but $\Delta \lambda_{\text{CD, max}}$ of AgHNPs is smaller than that of AgNHs (Figure 5.3e versus 5.7e). Third, $\Delta CD\%$ of AgNHs has irreversibility in the range of 50–133% and does not change symmetrically with alternating wetting/drying processes (Figures 5.7c, f and 5.8b, d). This illustrates that AgNHs have an irreversible water effect on the CD amplitude. The T- and L-plasmonic CD of AgNHs tends to quench with increasing $m$,
becoming saturated at $m > 7$ (Figures 5.7c, f and 5.8b, d). Although $\theta$ slightly decreases with increasing $m$, RH-AgNHs-215 and RH-AgHNPs-17 remain hydrophobic and hydrophilic, respectively (Figure 5.9). Hydrophobic AgNHs with low surface energy account for the irreversible water effect on chiroptical activity, and hydrophilic AgNHs with high surface energy cause the reversible water effect.

![Figure 5.9 Plot of water contact angle ($\theta$) versus $m$, in terms of RH-AgNHs-215 (blue spheres) and RH-AgHNPs-17 (red squares). Insets: photographs of water droplets applied to the sample surfaces, marked with the measured $\theta$.](image)

**5.3 Summary**

We neglect the helix geometrical limit of $P > d$ and operate GLAD under fast substrate rotation to generate AgHNPs having hidden helicity with nominal $P < d$. Stemming from the hidden helicity, the AgHNPs have intrinsic chiroptical activity at the LSPR wavelength of 370 nm. With increasing nominal $P$ in the range of 3–70 nm, the plasmonic mode tends not to shift but have a logarithmic increase in CD amplitude. The water effect on chiroptical activity of AgHNPs causes the plasmonic mode to redshift by $\sim$40 nm and amplify in CD amplitude by $\sim$140%, and is
markedly reversible in multiple alternating wetting/drying processes. However, the chiroptical activity of AgNHs with $P > d$ tends to be quenched by the multiple alternating wetting/drying processes, illustrating the irreversible chiroptical water effect. The reversible water effect is ascribed to the surface hydrophilicity of AgHNPs, and the hydrophobic AgNHs account for the irreversible water effect. The deposition is operated at regular $T_{sub}$ to avoid the integration of GLAD with an extremely low-$T_{sub}$ cooling system. Hence, this work introduces a cost-effective, facile approach to minimize plasmonic helix pitch to the molecule-comparable scale, paving the way to study chiral nanostructure approaching the physical limit and exploit significant chirality-related bioapplications to tackle important health and environmental problems. This work has been published in *Small* (2016, 12: 5902-5909).[84]
6 Plasmonic CD Generated by Chirality Transfer

6.1 Introduction

GLAD offers a one-step, wafer-scale fabrication, facile sculpture of helical structures, and general adaptation to a wide range of materials.\cite{46, 89} The latter two characteristics of GLAD enable one to adjust resonant CD of plasmonic nanohelices in the UV-visible-NIR regime. Given a $P$ of \(~50\, \text{nm}\), nanohelices composed of Cu, Au, Ni/Ag and Cu/Ag alloys (with 50:50 atomic ratio) exhibit resonant CD at a $\lambda$ of 750, 600, 500 and 480 nm, respectively.\cite{90} Cu nanohelices have a chiropical redshift of the longitudinal mode from 575 to 750 nm with an increase of $P$ from 20 to 100 nm.\cite{58} Ag nanohelices exhibit a pair of bisignate CD peaks located at 370 nm and in the visible region,\cite{68} ascribed to the transverse and longitudinal LSPR modes, respectively.\cite{84} The elongation of Ag nanohelices can barely shift the transverse CD mode, but cause the longitudinal CD mode to have a marked red shift.\cite{82}

Noble metals typically have engineerable LSPR and resonant CD in the visible region, but there is little report on the fabrication of chiral metamaterials with chiroptical activity at $\lambda < 300$ nm. Al has a melting point of 660.3 °C markedly lower than that of noble metals, so that it is of great difficulty to sculpture Al in the helical by GLAD, owing to temperature-enhanced adatom diffusion on the as-deposited AlNPs. It has been proposed to dope low-melting-point metal with a complementary metal to accomplish the helical sculpture by GLAD, e.g., doping 8% of titanium into magnesium (having a melting point of 650 °C) to produce Mg nanohelices.\cite{91} The doping-enhanced helical sculpture is ascribed to the prohibition of surface diffusion of adatoms, but is limited by an appropriate doping recipe for a given low-melting-point metal.

Herein, I devise a new method to deposit an achiral thin layer of Cu and Au on chiral silver NPs (i.e., AgHNPs) for generating chiroptical response via chirality transfer from the chiral host to the achiral guest. The chirality transfer can be generally adapted to diverse plasmonic metals, and the mechanism is elucidated. Moreover, the chirality-transfer approach overcomes the limit of helical sculpture of metals with low melting point, leading to a generation of chiroptically active plasmons.
excited from a wide range of metals of interest. This method is also suitable for low-melting metals such as aluminum.

6.2 Results and Discussion

I find out that the chirality transfer from chiral host to achiral guest generally occurs, for instance, from chiral AgHNPs to Cu (Figure 6.1a-c), from chiral CuHNPs to Ag (Figure 6.2), and from chiral AgHNPs to Au (Figure 6.1d-f). The deposition of the achiral guest was operated immediately after that of the chiral host in high vacuum, so that the host wasn't natively oxidized and there isn't a thin oxide layer at the host/guest interfaces. Some discussions are made for the chirality transfer.

Figure 6.1 Chirality transfer from the host of chiral AgHNPs (with a $P$ of ~4.5 nm and $H$ of ~40 nm) to the guest (with a nominal thickness of 30 nm) of (a-c) Cu and (d-f) Au, characterized by UV-visible spectra of (a, d) extinction, (b, e) CD, and (c, f) anisotropic $g$-factor: LH (red lines), RH (blue lines), the natively oxidized host of AgHNPs:AgO (solid lines), AgHNPs:AgO@guest (dotted lines), and AgHNPs@guest (dashes lines). AgO denotes the silver oxides with unknown stoichiometry. Green and cyan backgrounds highlight the spectra of the host and guest, respectively. (b) The ellipticity of the chiral host (solid lines) is amplified by 2 times for clarity.
First, in order to clearly observe the chiroptical induction, LSPR and resonance CD of chiral host should not overlap with those of achiral guest. Ag nanostructures have LSPR at a $\lambda$ of ~370 nm, and Cu and Au nanostructures have LSPR at a $\lambda$ of ~600 nm. For the CuHNPs@Ag, the LSPR of Ag barely occurs in the visible region with $\lambda > 500$ nm (Figure 6.2g), without overlap with that of the host CuHNPs.

Figure 6.2 Chirality transfer from the host of RH-CuNPs (with a $P$ of 3 nm and $H$ of 40 nm) to the guest of Ag (with a nominal thickness of 30 nm), characterized by UV-visible spectra of (a) extinction, (b) CD, and (c) anisotropic $g$-factor: the host of RH-CuNPs:CuO (dashed lines), and RH-CuNPs@Ag (solid lines). (b) The ellipticity of the chiral host (dashed line) is amplified by 5 times for clarity.
Second, without native oxidation of the host, the guest coating gives rise to the capping structures (Figure 6.3c, d, g, h). When the host is oxidized, the guest coating happens not only on the top of the host NPs but also in the gaps between the host NPs (Figure 6.3b, f).

Third, the guest capping gives rise to an amplification of the UV-visible extinction (Figure 6.1a, 6.1d, 6.2a) and that of chiroptical activity of the host arrays (Figure 6.1c, 6.1f, 6.2c, 6.4c). Fourth, a thickening of the guest (e.g., Au, Figure 6.4a) causes the chiroptical response of both the host
(e.g., chiral AgHNPs) and the guest to redshift (Figure 6.4b) and to be amplified (Figure 6.4c), but the host barely has a chiroptical red shift when the guest is thicker than 15 nm. It is illuminated that the host@guest method enables one to engineer the chiroptical activity of the host and guest by facilely tailoring the thickness of the guest layer.

Figure 6.4 Chirality transfer from the host of RH-AgHNPs (with a $P$ of ~4.5 nm and $H$ of ~40 nm) to the guest of Au, as a function of the nominal thickness of Au ($T_{Au}$). (a) UV-visible anisotropic $g$-factor spectra of RH-AgHNPs@Au, as a function of $T_{Au}$: 0 (black line), 10 (red line), 15 (blue line) and 30 nm (magenta line). Green and cyan backgrounds highlight the spectra of the host and guest, respectively. Plots of (b) $\lambda_{g,max}$ ($g$-factor peak position) and (c) $g_{max}$ ($g$-factor peak amplitude) versus $T_{Au}$, in terms of the host (green circles) and guest (cyan squares).

On the other hand, to solely study the contribution of plasmonic coupling, a layer of poly(methyl methacrylate) (PMMA) with a thickness of ~3 nm was uniformly coated on the host of RH-CuHNPs (Figure 6.6a and 6.5), to prohibit the helicity duplication from the chiral host to the capping guest. The 3-nm-thick PMMA layer would not eliminate the plasmonic coupling of the host and guest, if the plasmonic coupling existed. Note that before the coating of PMMA, the host was transiently exposed in the ambient environment while being transferred from the high vacuum GLAD chamber to the PMMA solution, so that the surface oxidation could be ignored. The coating of PMMA has a negligible effect on the chiroptical response of the host of RH-CuHNPs (red line versus black line, Figure 6.6b). Then the coating of Al on the RH-CuHNPs:PMMA doesn't cause the chiroptical activation in the $\lambda$ range of 250 – 500 nm (green line, Figure 6.6b). Similarly, a ~3-nm-thick PMMA (Figure 6.6c) can effectively eliminate the chirality transfer from the RH-AgHNPs to the guest Au at the $\lambda$ of ~600 nm (Figure 6.6d). It is
strongly illustrated that the plasmonic coupling has a negligible contribution to the chirality transfer.

Figure 6.5 (a) TEM and (b) cross-sectional SEM image of the host (LH-CuHNPs):PMMA nanostructures.

Figure 6.6 Elimination of chirality transfer by a shielding layer of PMMA: (a, b) from RH-CuHNPs (with a $P$ of 3 nm and $H$ of 40 nm) to the guest of Al; (c, d) from RH-AgHNPs (with a $P$ of 4.7 nm and $H$ of 43 nm) to the guest of Au. The nominal thickness of the guest is 30 nm. (a, c) TEM images of the host:PMMA structures. Inset in (c): cross-sectional SEM image of the host:PMMA structures. (b, d) UV-visible anisotropic $g$-factor spectra of the natively oxidized host (black lines), the host coated with PMMA (host:PMMA, red lines), and host:PMMA@guest (green lines).
As a result, a conclusion can be firmly drawn that the guest of achiral nanocappings duplicate the helical structures of the underneath chiral host, accounting for the generality of chirality transfer and chiroptical activation of the achiral guest. Thus it can be deduced that the native oxidation of the chiral host could give rise to an amorphous oxide layer to separate the helical host from the guest, resulting in deteriorating the helicity duplication and weakening the chiroptical induction of the nanocapping guest. The deduction is experimentally manifested in Figure 6.7. The native oxidation of the host of RH-AgHNPs (Figure 6.7a) tends to deteriorate the chirality transfer to the guest of Au nanocapping (red line versus blue line, Figure 6.7b). Note that the amorphous AgO (with unknown stoichiometry) can be crystalized under an exposure to the electrons during TEM characterization, but PMMA will not. Consequently, the amorphous layer partially crystallized in the TEM characterization (highlighted by the dashed circle, Figure 6.7a) is assigned to the native oxide AgO, and the amorphous coating (Figure 6.6c) is assigned to PMMA. The host oxidation-caused weakening of the chiroptical induction also occurs in the chiral AgHNPs@Cu (dotted lines versus dashed lines, Figure 6.1c).

![Figure 6.7](image)

**Figure 6.7** Native oxide-induced weakening of chirality transfer from the host of RH-AgHNPs (with a $P$ of ~4.5 nm and $H$ of ~40 nm) to the guest of Au (with a nominal thickness of 30 nm). (a) TEM image of a RH-AgHNPs:AgO, and the dashed circle highlights AgO that were crystallized after exposure to the electron beam during TEM characterization. (b) Anisotropic $g$-factor spectra of RH-AgHNPs:AgO (black line), RH-AgHNPs:AgO@Au (red line), and RH-AgHNPs@Fu (blue line). Green and cyan backgrounds highlight the spectra of the host and guest, respectively.
6.3 Summary

This work demonstrates a new methodology of chirality transfer from chiral host to achiral guest, leading to inducing chiroptical activity of the achiral guest made of some plasmonic materials that aren’t facilely sculptured in the helical to exhibit chiroptical activity. The new methodology effectively broadens the material range of plasmonic chiral nanostructures, to excite nanoplasmons with UV-active chiroptical activity on resonant with the irradiation absorption of life building blocks. It has been proposed that UV-active plasmons with chiroptical activity can be used to resonantly enhance the UV absorption of biomolecules under CPL excitation, leading to an amplification of Raman optical activity, i.e., surface enhanced Raman optical activity (SEROA). It would open a door to develop chiroptical spectroscopies for sensitively detecting absolute configuration that is of urgent interest in studying stereobiochemical conformation and bio-interactions that are of crucial, substantial importance to understand a wide range of homochirality-determined biological phenomena. Furthermore, the chiral host@achiral guest methodology enables one to integrate two or more plasmonic materials for synergistically producing nanoplasmons with tailorable, broadband, strong chiroptical activity in the UV-visible-NIR region, which is of prominent interest in investigating a wide range of nanoplasmon-induced studies, such as photocatalyses, photocatalytically asymmetrical syntheses, bio-detection and bio-imaging. This work has been published in Small (2017, DOI: 10.1002/smll.201701112).
7 Conclusions and Perspective

7.1 Conclusions

In this dissertation, I present my study of two methods to enhance enantiodifferentiation characterized by ECD. It is of fundamental significance to differentiate an enantiomer from its mirror image (i.e., enantiodifferentiation), through monitoring the OA of enantiomers, which is typically characterized by ECD/CD in the UV-visible region. However, sub-wavelength molecular dimensions prevent enantiomers from effectively perceiving different circular polarization states, leading to low enantiomeric OA and weak enantiodifferentiation. Some approaches have been developed to amplify enantiomeric OA on the basis of the emerging chiral metamaterials of metallic HNPs.

Given the chirality-related complexity in chiral molecule–metallic helical nanoparticle interactions, it is necessary to understand achiral molecule–metallic helical nanoparticles. First, I use GLAD to deposit Ag HNPs with a helical pitch ($P$) of ~200 nm larger than the wire diameter ($d$) of ~45 nm of the helix, i.e., AgNHs. AgNHs exhibit strong plasmonic CD composed of a broadband longitudinal mode (i.e., L-mode) in the visible region, a transverse mode (i.e., T-mode) at a wavelength of ~370 nm, and a dielectric mode in the deep UV region (at a wavelength shorter than 320 nm). The CD spectrum flips around the zero-CD axis while the helicity of AgNHs switches. When Ag nanostructures lack helicity and appear as nanorods, the chiroptical response disappears. This illustrates that chiroptical activity intrinsically stems from structural helicity. The adsorption of alkyl ligands (CH$_3$(CH$_2$)$_6$CH$_2$-G or C$_8$-G, where G is –H, –COOH, –NH$_2$ and –SH) on AgNHs markedly weakens the two plasmonic CD modes, and the T-mode is weakened more seriously than the L-mode. The deterioration of the plasmonic CD is exacerbated as the bonding energy of the Ag-alkyl ligand contacts increases, which is attributed to the increase in the dielectric constant of the AgNHs ($\varepsilon_r$) medium and the electron withdrawal from the AgNHs toward the alkyl ligands. Derived from the ligand-induced weakening of the plasmonic CD, enantiodifferentiation of L-Glutathione (L-GSH) from D-GSH is dramatically enhanced. The chiroptical weakening sensitivity varies with the absolute configuration of GSH, resulting in an enantiodifferentiation anisotropic $g$ factor of ~0.5 that is independent of AgNH helicity. The AgNH-induced anisotropy
g factor is superior to those obtained by other methods, by 2-4 orders of magnitude. It is the largest achieved to date, and as high as one-quarter of the theoretical maximum. These works contribute to devising a simple method to quantitatively study metallic helical nanoparticle–molecule interactions. Furthermore, the method can be generally adapted to differentiating chiral molecules in biological systems. The interaction substantially stems from the formation of metal-ligand contacts, including ligands terminating with –NH₂ and –COOH that are typically contained in amino acids. Proteins are composed of 20 kinds of amino acids that all have homochiral L-configurations. This homochirality leads to chirality-dependent interactions between biological systems and chiral drugs/pesticides. Given the quick development of drug carriers based on plasmonic nanoparticles, this work provides an additional degree of freedom in terms of chiroptical activity to study the biological functions of chiral drugs and pesticides, paving the way to develop a wide range of chirality-related applications in the areas of pharmaceutical and agricultural production, food quality control, disease diagnosis and treatment, and environmental protection.

Second, I operate GLAD with fast substrate rotation to reduce P to less than d, and generate AgHNPs that exhibit negligible dielectric CD in the deep UV region, offering a helical substrate to directly amplify the optical activity of enantiomers grafted on AgHNPs. Enantiomer 1 ((R)- and (S)-1,1′-Binaphthyl benzo-27-crown-8 benzyl (1, 2-dithiolan-3-yl) pentanoate) and Enantiomer 2 ((R)- and (S)-1,1′-Binaphthyl-2,2′-dithiol) were deliberately chosen as they do not have optical excitation that coincides with a resonance of the AgHNPs, to eliminate the possibility of observing a plasmonic resonant enhancement. The anchoring of enantiomers on AgHNPs with sub-5 nm P leads to the enantioselective amplification of the enantiomeric OA by roughly tenfold; the LH- and RH-AgHNPs amplify the optical activity of Enantiomer 1 and Enantiomer 2, respectively. This result is ascribed to the change in the dihedral angle of enantiomers adsorbed on AgHNPs. Such enantioselective amplification tends not to occur when P > 5 nm.

Given the enantiodifferentiation of biomolecules that are typically dissolved in an aqueous solution, the water effect on the optical activity of AgHNPs causes the plasmonic mode to redshift by ≈ 40 nm and amplify in CD amplitude by ≈140%. It is markedly reversible in multiple alternating wetting/drying processes. This is ascribed to the surface hydrophilicity and low array porosity. However, the chiroptical activity of AgNHs with P > d tends to be quenched by the
multiple alternating wetting/drying processes, illustrating the irreversible chiroptical water effect. The reversible water effect is ascribed to the surface hydrophilicity of AgHNPs, and hydrophobic AgNHs account for the irreversible water effect.

I devise a new methodology to generate plasmonic CD through chirality transfer from chiral host to achiral guest, owing to the helicity duplication of the achiral guest from the chiral host. This leads to the inducing of chiroptical activity for the achiral guest made of plasmonic materials that are not easily sculptured in the helix. It has been proposed that UV-active plasmons with chiroptical activity can be used to resonantly enhance the UV absorption of biomolecules under CPL excitation, leading to an amplification of ROA, i.e., surface-enhanced ROA. This opens the door to the development of chiroptical spectroscopies for sensitively detecting absolute configurations, which is of urgent interest in studying stereobiochemical conformation and biointeractions. These interactions are of crucial importance to understanding a wide range of homochirality-determined biological phenomena. Furthermore, the chiral host-achiral guest methodology enables one to integrate two or more plasmonic materials to synergistically produce nanoplasmons with tailorable, broadband, strong chiroptical activity in the UV-visible-NIR region, which is of great interest for a wide range of nanoplasmon-induced studies, such as studies of photocatalyses, photocatalytically asymmetrical syntheses, biodetection and bioimaging.

7.2 Perspective

In Chapters 3 and 4, I demonstrated two methods of enhancing enantiodifferentiation using Ag helical structures. These methods require molecules terminated with a functional group (i.e., –NH₂, –SH and –COOH) that can be grafted onto silver. The use of silver nanoparticles as a medium to study enantiodifferentiation, to some extent, some molecules without functional group are limited.

For example, a chiral molecule, Flavin mononucleotide (FMN), has radiative absorption at a wavelength of 220, 265, 370 and 450 nm. RH-AgHNPs with a nominal pitch of 4 nm and height of 40 nm have LSPR and resonant CD at 370 and ~450 nm, but barely shows chiroptical activity at wavelengths shorter than 330 nm. The FMN coating on the RH-AgHNPs leads to detection of molecular CD at 220 and 265 nm, which is dramatically amplified from FMN solutions (red versus
blue lines, Figure 7.1c). This shows that chiral AgHNPs contribute to enhancing the chiroptical activity of FMN.

Two mechanisms may account for the surface enhancement. One is the surface-induced aggregation of chiral molecules; the other is the enhancement of the optical chirality of CPL by AgHNPs. To solely study the first mechanism, the plasmonic material of chiral NPs will be replaced with non-plasmonic material, such as TiO₂. If the chiroptical enhancement of FMN could be observed on the surface of TiO₂HNPs, it could be deduced that the surface-induced aggregation of plasmons make an important contribution to the surface enhancement of molecular chiroptical activity. As the surface-induced enhancement is closely relate to the surface area, the helical structures of TiO₂HNPs are tailored to optimize molecular chiroptical enhancement. If there is no chiroptical enhancement of TiO₂HNPs, AgHNPs are suggested to play an essential role in enhancing the chiroptical activity of FMN. Chiroptical enhancement will be studied and optimized as a function of FMN concentration and the helical structures of chiral AgHNPs.

Figure 7.1 UV-visible spectra of (a) extinction, (b) CD and (c) g-factor spectra: 0.2 mmol/L FMN solution (blue lines), RH-AgHNPs with a nominal pitch of 4 nm and height of 40 nm (black lines), FMN coating (0.2 mmol/L, 100 ul) on the RH-AgHNPs (red lines). (d) FMN molecular structure. Inset: (c) g factor spectra in λ of 200-300 nm of 0.2 mmol/L FMN solution.

In addition, the optical activity of plasmonic nanostructures depends on the shape and material of the structure. If other metals (gold and copper) are used instead of silver, does the enhancement
factor increase? I will study this question in the future. I also plan to fabricate a variety of nanostructures that are suitable for the study of enantiodifferentiation for various enantiomers by adjusting the structure and materials of the nanostructures. This will open the door to using surface-enhanced chiroptical spectroscopes for the sensitive detection of absolute configuration and stereoisometric conformation, to study a wide range of important biological interactions and phenomena.
References


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Publication list


3. Wai-Fung Lau#, **Lin Yang**#, Fai Bai and Zhifeng Huang,* Weakening Circular Dichroism of Plasmonic Nanospirals Induced by Surface Grafting with Alkyl Ligands *Small*, 12, 6698 (2016) [#equally contributing to the work]


Conferences


2. “Plasmonic Nanoparticles with Reversible Aqueous Solvent Effect on Intrinsic Chiroptical Activity”, Young Giants of Nanoscience 2016, Hong Kong-Poster presentation

3. “Ultraviolet-Visible Chiroptical Activity of Aluminum Nanostructures” Gordon Research Conferences 2017, Hong Kong-Poster Presentation

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