Optical properties of chiral plasmonic nanoparticles and mesoporous silicon nanowires

Junjun Liu

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Optical Properties of Chiral Plasmonic Nanoparticles and Mesoporous Silicon Nanowires

LIU Junjun

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)

September 2017
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.

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Date: September 2017
Abstract

Structural engineering plays an essential role in controlling the optical properties of nanostructures, which are of fundamental and practical interest in nanoscience and technology. In this study, two kinds of nanostructural engineering were investigated systematically to enrich nano-optics research: structural helicity was imposed on plasmonic nanoparticles (NPs) with chiroptical activity engineerable in the ultraviolet (UV)–visible region, and porosification was imposed on silicon nanowires (SiNWs) to tune optical interaction and photoluminescence (PL).

The generation of helical metamaterials, which have strong, engineerable chiroptical activity in the UV–visible region, has attracted increasing attention due to the manipulation of the circular polarization state of light to develop diverse homochirality-associated bio-applications. Glancing-angle deposition with fast substrate rotation is performed to generate plasmonic helical NPs (PhNPs) with a helical pitch ($P$) of less than 10 nm, which is so much smaller than the wire diameter ($d$) that the PhNPs appear to be achiral NPs. The PhNPs exhibit chiroptical activity that originates intrinsically from hidden helicity, characterized by circular dichroism (CD). With an increase of $P$ from 3 to 66 nm, the plasmonic CD signals barely shift but show a logarithmic amplification. PhNPs made of aluminum, silver, and copper exhibit a stable chiroptical response from the deep UV (~220 nm) region to the visible region. When an achiral plasmonic nanostructure guest is coated on a PhNP host (i.e., a chiral host@achiral guest nanostructure is created), the achiral guest becomes chiroptically active due to helicity transfer from the chiral host to the achiral guest. Such a helicity transfer can be generally adapted to diverse plasmonic metals to tailor the plasmonic chiroptical response flexibly in the UV–visible region. Furthermore, an amplification of the near-field optical chirality induced by the PhNPs would pave a novel way to performing asymmetric syntheses, for which investigations are currently lacking. Silver PhNPs are used to effectively
mediate the enantioselective photocyclodimerization of 2-anthracenecarboxylate: left-handed silver PhNPs lead to a positive $ee$ (enantiomeric excess) value, and right-handed silver PhNPs give rise to a negative $ee$ value. The enantioselectivity is enhanced with a decreasing $P$. The PhNP-mediated enantioselective photocyclodimerization is ascribed to the synergistic contribution from chirally helical surface-induced enantioselective adsorption of 2-anthracenecarboxylate and chiroptically active nanoplasmon-enhanced optical chirality of near-field circularly polarized light.

Metal-assisted chemical etching (MACE) is carried out to generate mesoporous SiNWs (mp-SiNWs) with mesopores from 2 to 50 nm. The porosification imposes two prominent properties onto SiNWs: a high surface-to-volume ratio and quantum confinement ascribed to the shrinkage of silicon skeletons. Hence, engineering the porosity of SiNWs is of fundamental importance. Here, a new method is devised to reduce the porosity of mp-SiNWs without changes in the MACE conditions. After generating the mp-SiNWs with high porosity, the mp-SiNWs are removed from the mother Si wafers with sticky tape, followed by MACE under the same conditions to produce low-porosity mp-SiNWs. Less porous mp-SiNWs reduce optical scattering from the porous Si skeletons and vertically protrude on the wafer without aggregation to facilitate optical trapping. Consequently, low-porosity mp-SiNWs effectively reduce UV–visible reflection loss. Furthermore, optical applications require surface modification of mp-SiNWs with functional chemicals, which has a prerequisite to passivate mp-SiNWs with H-termination using 5% hydrogen fluoride. 40% NH$_4$F, which has been widely used to passivate Si(111) wafers with H-termination, tends to unexpectedly etch mp-SiNWs attributed to surface F-termination caused by the nucleophilic attack of F$^-$ anions to Si atoms. It has been used to study systematically the NH$_4$F-etching rate as a function of the doping levels of SiNWs, surface crystalline orientations, and porosity. At a modest temperature of 110°C, 1,4-diethynylbenzene (DEBZ) is grafted via monosilylation grafted on
H-terminated mp-SiNWs. The modified mp-SiNWs with chemically active monolayers is facilely subjected to further chemical modification and surface functionalization. In addition, the monosilylation encodes mp-SiNWs with PL of DEBZ, opening a door to flexible engineering of PL of mp-SiNWs for optoelectronic and bio-detection applications.
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First of all, I would like to thank my supervisor, Dr. Zhifeng Huang for his support and supervision during my doctoral period. He teaches me how to pursue an ambitious idea through combining a tiny experimental phenomenon with a lot of academic background investigation, and transform an idea to a systematic and solid academic work. He also educates me the importance of persistence and concentration to achieve works, and the need of thinking outside of the box and thinking from the view of “the whole big tree”. The sensitivity to the novel ideas and necessary characteristics to be a researcher I learn from him would stimulate me to pursue a higher level in my future academic research.

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List of Abbreviations

AlNP Aluminum nanoparticle
ATR-FTIR Attenuated total reflection Fourier-transform infrared spectroscopy
AC 2-anthracenecarboxylate
AgNP Silver nanoparticle
AgNR Silver nanorod
AgNH Silver nanohelix
CD Circular dichroism
CB Circular birefringence
CuNP Copper nanoparticle
CTAB Cetyl trimethylammonium bromide
CPL Circularly polarized light
DEBZ 1,4-diethynylbenzene
ee Enantiomeric excess
FDTD finite-difference time-domain
GLAD Glancing angle deposition
HPLC High-performance liquid chromatography
HT head-to-tail
HH head-to-head
LSPR localized surface plasmon resonance
LCP Left-handed circularly polarized light
LH Left-handed
LP Linear polarized light
MACE Metal-assisted chemical etching
NH₄F Ammonium fluoride
ORD Optical rotatory dispersion
PhNP Plasmonic helical nanoparticle
PL Photoluminescence
RCP Right-handed circularly polarized light
RH Right-handed
SiNWs Silicon nanowires
SEM scanning electron microscopy
TEM Transmission electron microscopy
XRD X-ray diffraction crystallography
XPS X-ray photoelectron spectroscopy
3D Three-dimensional
List of Figures

Chapter 1

Figure 1.1 (a) Linearly polarized light (blue) can be divided into equal contributions of RCP (red) and LCP (green). (b) Circular birefringence (CB) (or optical rotatory dispersion) causes one component of CPL to propagate faster than the other, so that the plane of the electric-field vector rotates by an angle $\Phi$. (c) In CD, one component of CPL is absorbed more strongly than the other, leading to net polarization ellipticity at an angle $\theta$. 

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Chapter 2

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Chapter 3

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Chapter 1 Introduction

Nanoscience and nanotechnology have attracted growing interest in fundamental research and industrial applications in the past decade. Nanostructures, which are defined as having one dimension less than 100 nm, are essential to nanoscience and nanotechnology and have become one of the hottest topics in multiple research fields. In particular, one-dimensional (1D) nanostructures such as nanoscale wires, rods, tubes, and belts have become widely investigated for their diverse fabrication methods and variable properties, including size, shape, and constituent materials.

Fabrication of helical metamaterials to study chiral plasmonics\textsuperscript{2-3} has attracted considerable recent attention because of their extremely strong chiroptical activity, which are able to manipulate the polarization state of light and are widely required in several applications, such as circularly polarizing beam splitters,\textsuperscript{4} broadband circular polarizers,\textsuperscript{5} quarter-wave plates,\textsuperscript{6} and sensitive biosensors.\textsuperscript{7} In an improvement from other helix fabrication techniques, glancing-angle deposition (GLAD)\textsuperscript{8-10} provides one-step, wafer-scale production of helical metamaterials on various kinds of substrates, paving the way for functional devices. A helix is geometrically described by helical pitch ($P$), coil diameter ($D$), wire diameter ($d$), number of helical pitch ($n$), and height ($H = nP$). However, the geometric prerequisite for forming a helix is that $P$ should be greater than $d$. With the limitations of the current development of nanofabrication techniques, it is difficult to minimize $d$ and consequently $P$ to the sub-10-nm molecule-comparable scale, which prevents the study of chiral plasmonics at dimensions approaching the physical limit.

Biomolecules typically absorb ultraviolet (UV) light with a wavelength ($\lambda$) shorter than 250 nm, but they usually have such a sub-wavelength size that they can barely perceive the circular polarization of circularly polarized light (CPL), which leads to
low chiroptical activity. To effectively enhance the biomolecules’ chiroptical activity, it has been proposed to amplify an optical chirality (denoting chirality density) of CPL in the UV range to enhance the biomolecules’ CPL absorption. Numerical simulation reveals that chiral metamaterials can resonantly enhance the optical chirality of CPL in the vicinity of their surfaces at a wavelength corresponding to the localized surface plasmon resonance (LSPR), which therefore results in a fundamental demand on the production of chiral metamaterials with LSPR and chiroptical activity (i.e., resonant circular dichroism [CD]) in the UV region.

On the other hand, as one of the most widely investigated 1D nanomaterials, silicon nanowires (SiNWs) appear to be solid long cylinders with integrated semiconducting properties. Since 2009, it has been reported that SiNWs could be electrochemically porosified to create mesoporous SiNWs (mp-SiNWs) with pores between 2 and 50 nm. Compared with solid SiNWs, mp-SiNWs integrated the 1D nanostructures with two porosification-induced effects that included an increased surface area ratio of the porous profile and quantum confinement derived from shrinkage in the residual Si skeletons, which have recently undergone intensive study. Derived from structural porosification, the enhanced surface-to-volume ratio generates enormous voids for mass storage and transportation that have been developed for a wide range of applications, including energy storage, lithium ion batteries, drug delivery, gas sensors, photocatalysis, and encryption. Metal-assisted chemical etching (MACE) has been mainly used to create mp-SiNWs in a simple, inexpensive way, and the porosification of SiNWs gives rise to investigation of the optical properties of mp-SiNWs, especially photoluminescence (PL) and antireflection. Therefore, it is of fundamental significance to engineer the porosity of SiNWs to optimize the functional performance in various applications. The ability to control and simplify the engineering of the porosity of mp-SiNWs is just beginning. Meanwhile, the promoted applications such as energy storage, photocatalysis, and PL demand substantial surface modification of SiNWs with
functional chemicals to subtly tune the surface state–related electronic band structures.

In this dissertation, neglecting the geometric limit of helices, I present GLAD with fast substrate rotation to generate helical silver NPs (AgNPs) with $P < d$ and chiroptically active in the UV–visible region. The nominal $P$ can be minimized as small as 3.5 nm, where AgNPs still have a reliable and detectable chiroptical response. I then use such an approach to produce chiral Al nanostructures that exhibit strong chiroptical activity in the deep UV–visible region, which has significance for further investigation of the interaction between chiral plasmonics and biomolecules. Furthermore, helical AgNPs are used to mediate an asymmetric synthesis, enantioselective photocyclodimerization of 2-anthracencarboxylate (AC). For mp-SiNWs, PL and reflection loss are engineered by controlling the porosity of mp-SiNWs and surface modification.

1.1 Plasmonic helical nanoparticles (PhNPs)

1.1.2 Chirality

Chirality, a natural feature in which an object cannot be superimposed onto its mirror image, has substantial relevance to the origin of life and biological functions. Nature generally adopts helical structures to express chirality, from the mega (e.g., galaxy) to macro (e.g., snail shells$^{24}$ and honeysuckle winding around its support), micro (e.g., bacterial colonies), supramolecular (e.g., DNA and peptides), molecular (e.g., enantiomers), and atomic scales. Chirality also exists in CPL.

1.1.3 Chiroptical activity

A chiral object will have a differential interaction with left-handed and right-handed
CPL (LCP and RCP). Taking chiral drugs as an example, in the pharmaceutical industry, distinction between two enantiomers has great importance for drug development. The effect of one enantiomer in a drug could differ greatly from that of another enantiomer. In the 1960s, a tragedy occurred from the use of thalidomide; the \((R)\)-enantiomer is effective against insomnia and morning sickness but the \((S)\)-enantiomer causes limb deformation in newborns. The probing techniques used to differentiate the enantiomers are therefore of great importance. The techniques are based on different interactions of enantiomers with LCP and RCP, and the difference is referred to as “chiroptical activity.” In terms of electronic bands, chiroptical activity can be characterized in the UV–visible–near infrared (NIR) region by CD to monitor the differential absorption of LCP and RCP and by optical rotatory dispersion to monitor the differential phase propagation velocity of LCP and RCP. The origin of the natural chiroptical activity is shown in Figure 1.1.\(^{25}\) Moreover, CD spectroscopy can also provide the information for the structural conformation of a molecule,\(^{26}\) so it was selected as the primary method in my studies for detection of the signal of chiral plasmonic NPs.

Figure 1.1(a) Linearly polarized light (blue) can be divided into equal contributions of RCP (red) and LCP (green). (b) Circular birefringence (CB) (or optical rotatory dispersion) causes one component of CPL to propagate faster than the other, so that the plane of the electric-field vector rotates by an angle \(\Phi\). (c) In CD, one component of CPL is absorbed more strongly than the other, leading to net polarization ellipticity at an angle \(\theta\).\(^{25}\)
1.1.4 CD spectroscopy

CD is the differential absorption of LCP and RCP by chiral media, which is defined by the following equation,

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

where \( A_{LCP} \) and \( A_{RCP} \) are the absorptions of LCP and RCP, respectively. \( \Delta A \) is a function of wavelength, which can also be expressed by applying Beer’s law as,

\[ \Delta A = \Delta \varepsilon C l = (\varepsilon_{LCP} - \varepsilon_{RCP}) C l \] (1.2)

where \( \varepsilon_{LCP} \) and \( \varepsilon_{RCP} \) are the molar extinction coefficients for LCP and RCP light, \( C \) is the molar concentration, and \( l \) is the path length in centimeters.

Although \( \Delta A \) is usually measured, for historical reasons, CD is usually reported in degrees of ellipticity \( \theta \).

This relationship is derived by defining the ellipticity of the polarization as:

\[ \tan \theta = \frac{E_R - E_L}{E_R + E_L} \] (1.3)

where \( E_R \) and \( E_L \) are the magnitudes of the electric-field vectors of the RCP and LCP, respectively (Figure 1.2).

Generally, \( \tan \theta \) is small and can be approximated as the angle \( \theta \) in radians. Because the intensity of light, \( I \), is proportional to the square of the electric-field vector, the ellipticity becomes,

\[ \theta (\text{radians}) = \frac{(I_R^{1/2} - I_L^{1/2})}{(I_R^{1/2} + I_L^{1/2})} \] (1.4)

According to Beer’s law,

\[ I = I_0 e^{-\alpha n l_0} \] (1.5)
Figure 1.2 Elliptical polarized light (violet) is composed of unequal contributions of RCP (blue) and LCP (red).

The ellipticity can then be written as,

\[ \theta \text{ (radians)} = \left( \frac{-\Delta A_{\text{In10}} - e^{-\frac{\Delta A_{\text{In10}}}{2}}}{e^{-\frac{\Delta A_{\text{In10}}}{2}} + e^{-\frac{\Delta A_{\text{In10}}}{2}}} \right) = \frac{e^{\frac{\Delta A_{\text{In10}}}{2}} - 1}{e^{\frac{\Delta A_{\text{In10}}}{2}} + 1} \] (1.6)

Because \( \Delta A << 1 \), after expanding the exponentials and neglecting the high-order terms, eq. (1.6) leads to

\[ \theta \text{ (degrees)} = \Delta A \left( \frac{\Delta A_{\text{In10}}}{4} \right) \left( \frac{180}{\pi} \right) \] (1.7)

then combining eq. (1.2) and eq. (1.7),

\[ \theta \text{ (mdegrees)} = 32982 \Delta \varepsilon \text{Cl} \] (1.8)

Therefore, instead of \( \Delta A \), CD spectra are usually studied in terms of ellipticity.

1.1.5 Dissymmetry g-Factor

Another useful quantity g-factor is introduced to quantify and normalized the chiral effect among various chiral materials and is defined as,
\[ g = 2 \frac{\Delta A}{A} = 2 \frac{A_{LCP}-A_{RCP}}{A} \quad (1.9) \]

where \( A \) is the total absorption of non-polarized light.

Compared with CD, \( g \)-factor can more exactly demonstrate the capacity of a chiral material to induce a chiral field. However, like the CD spectrum, the \( g \)-factor is still a far-field effect and cannot illustrate the details of the near-EM field of chiral materials. Otherwise, optical chirality, which is equivalent to the chiral density of an electromagnetic (EM) field, can show the enhancement degree of the chiroptical activity of chiral molecules surrounded by plasmonic nanostructures.

Optical chirality is applied to parameterize the chirality density of EM field, which is defined as

\[ C = \frac{\varepsilon_0}{2} \mathbf{E} \cdot \nabla \times \mathbf{E} + \frac{1}{2\mu_0} \mathbf{B} \cdot \nabla \times \mathbf{B} \quad (1.10) \]

where \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of free space, respectively, and \( \mathbf{E} \) and \( \mathbf{B} \) are the local EM field.

### 1.1.6 Nanoplasmonics with chiroptical activity

Metamaterials are artificial composite materials with sizes and spacing much smaller than the wavelength of interest. When the nanostructures are metallic, the field of nanoplasmonics is entered, which studies the optical phenomena of the metal nanostructures in the nanoscale.

When a metal NP in a dielectric medium is illuminated by an EM wave, the free electrons in the metal will oscillate as a response to the electric field of the EM wave, which is known as surface plasmon. LSPR is the interaction between the NPs’ surface electrons and incident light confined on the NP surface shown in Figure 1.3. When the NPs are far smaller than the light’s wavelength, the surface
electrons of the NPs collectively oscillate with the light transmission. When the oscillation frequency of electrons and photons is matched, the plasmon resonance occurs.28

![Figure 1.3 Principle of LSPR: the interaction between surface electrons of NP sphere and incident light.28](image)

As a subset of metamaterials, chiral metamaterials have attracted much attention because of their extremely strong optical activity; they are able to manipulate the polarization state of light, which is widely required in several application fields, such as circularly polarizing beam splitters,4 broadband circular polarizers,5 quarter-wave plates,6 and sensitive biosensors.7

In nature, the essential amino acids, carbohydrates, nucleic acids, and proteins all show chirality, but it should be noted that the chiroptical response of most biomolecules is generally inherently weak.

In contrast, plasmonic chiral metamaterials have attracted great interest because their chiroptical effects can be several orders of magnitude greater than those of common biomolecules.29-30 Furthermore, chiral plasmonic metamaterials have the ability to achieve negative refraction by means of chirality31 or to artificially reproduce and enhance the weak chiroptical effects present in natural chiral molecules.14
Circular polarization manipulation in the UV–visible–NIR region has attracted increasing attention due to the intensive desire for advanced optical displays and chirality-determined bio-applications. To perform the optical manipulation, it is critical important to tailor the chiroptical activity of chiral metal materials in the UV–visible–NIR region.

Plasmonic chiral metamaterials are commonly classified according to the fabrication methods (top-down or bottom-up). However, to thoroughly investigate the chiroptical activity manipulation of the LSPR, I herein classify the chiral plasmonic nanostructures according the LSPR wavelength region.

1.1.6.1 Infrared region

A uniaxial photonic metamaterial composed of 3D gold helices was investigated in 2009 as a compact broadband circular polarizer in the mid-infrared regime. These gold helices were fabricated with an approach based on direct laser writing of helical pores followed by electrochemical deposition of gold (Figure 1.4a). These measured transmittance spectra from 3.5 to 7.6 μm reveal the anticipated blocking one direction of CPL, whereas transmitting the other CPL (Figure 1.4b,c).

![Figure 1.4](image)

Figure 1.4 (a) Fabrication process of 3D helices by direct laser writing and electrochemical deposition of gold. (b) Experimental and (c) calculated transmission spectra in the mid-infrared region for two-turn right-handed gold helices with RCP (blue) and LCP (red).

Stacked-planar structures are an alternative approach to achieving strong chiroptical activity. In Figure 1.5a, the authors studied metal-dimers consisting of a stack of
two identical twisted split-ring resonators analogous to stereomaterials in chemistry. The transmittance spectrum of this twisted split rings chiral structures can be tuned by adjusting the twisting angle. For the 90° twisted dimer in Figure 1.5a (middle), the magnetic dipoles in the two split rings at the two resonances ($\omega_90^-$ and $\omega_90^+$) are aligned parallel and antiparallel to produce chiroptical responses in the infrared region in Figure 1.5a (right). Similarly, diverse stacked chiral nanostructures have been created based on this method. In Figure 1.5b, a strong chiroptical effect was observed from photonic metamaterials that consist of an array of twisted-arc double layers located from 1.1 to 1.6 $\mu$m.33 Here another 3D arrangement of NPs in a handed fashion with resonance plasmonic coupling provides enhanced chiroptical responses in plasmonic oligomers.34

Figure 1.5 (a) Schematic of the dimer metamaterials (left). Oblique views of 90° twisted gold split rings (middle). Experimental transmittance spectra of twisted gold split rings (right). The black and red curves represent experimental and simulated results, respectively.32 (b) Twisted-arc chiral metamaterials and their corresponding transmittance spectra.33 (c) CD spectra and scanning electron microscopic (SEM) images of three chiral oligomers.34
1.1.6.2 Visible region

LSPR is sensitive to the materials’ and nanostructures’ size,\textsuperscript{35} so when the NPs’ size changed to nanoscale or the fabricated materials were changed from gold to silver, the LSPR of chiral plasmonic metamaterials shifted to the visible region. GLAD is a unique physical vapor deposition performed at a large glancing deposition angle $\theta$ between the incidence of the vapors and the direction of the substrate normal, which is typically greater than $75^\circ$. After the initial nucleation of condensed adatoms on a substrate, the self-shadowing effect induced by the oblique deposition causes the deposited nanostructures to be spatially separated. The clockwise/counterclockwise rotation of the substrate gives rise to a sculpture with right/left-handed helicity. When nucleation occurs on periodic patterns (e.g., Au nanodots patterned by micellar nanolithography), a periodic array of plasmonic NHs with well-defined helical structures can be deposited over a large area (Figure 1.6).\textsuperscript{8} The LSPR of the CD spectra is located in the visible region.

![Figure 1.6 GLAD of nanohelices on (a) prepatterned Au nanodots by micellar nanolithography, (b) nanohelix fabrication process. (c) CD spectra of two handedness nanohelices. Inset: transmission electron microscopic (TEM) images of grown structures with left (top) and right (bottom) chirality.\textsuperscript{8}](image)

In recent years, our group has systematically studied the CD spectra of silver nanostructures generated by GLAD. In Figure 1.7, homochiral co-axial silver nanohelices were fabricated by GLAD with one or multiple full-pitch with left and right handedness.\textsuperscript{36} Figure 1.7(g) shows the CD of a homochiral co-axial array
changed with tailoring $n$, in which the CD amplitude is normalized by $n$. The CD spectra are composed of two bisignated peaks, one in the UV regime and the other in the visible regime. The chiroptical activity in the UV regime barely varies with $n$, in terms of the CD and peak position. In contrast, in the visible regime, an increase of $n$ significantly reduces the CD and leads to the LSPR blue-shift, which indicates that the chiroptical activity in the UV regime differs from that in the visible regime.

Figure 1.7 GLAD of homochiral AgNH arrays, with left (L: a, c, e) and right (R: b, d, f) handedness. AgNHs have helical pitch ($P$) of approximately 200 nm, and the number of pitch ($n$) is 1 (a, b), 2 (c, d), and 3 (e, f). (g) CD spectra of homochiral AgNH arrays with tailoring the $n$.36
Figure 1.8 Chiroptical activity of heterochiral bi-axial AgNH arrays, as a function of the direction of optical incidence. SEM images: (a) bi-(1L+1R); (b) bi-(1R+1L). Insets: schematics and SEM images of the heterochiral structures. CD spectra: (c) bi-(1L+1R), (d) bi-(1R+1L).

In addition to engineering the CD in terms of $n$, studies on tailoring the chiroptical activity of incorporation of the left- and right-handed helices of forming heterochiral bi-axial and co-axial Ag nanohelices have also been performed (Figure 1.8 and Figure 1.9). For a bi-axial structure with two incorporated helix axes, the CD in the visible region changes sign when switching the direction of optical incidence, which can function as a circular polarizer in the visible spectrum. On the contract, the co-axial structures do not extinguish the chiroptical activity.

Figure 1.9 Chiroptical activity of heterochiral co-axial AgNH arrays, as a function of the direction of optical incidence. SEM images: (a) co-(1L+1R); (b) co-(1R+1L). Insets: schematics and SEM images of the heterochiral structures. CD spectra: (c) co-(1L+1R), (d) co-(1R+1L).

GLAD can be generally adapted to a wide range of materials, which enable one to adjust the resonant CD of plasmonic nanohelices in the UV–visible–NIR regime. Given a $P$ of approximately 50 nm, nanohelices composed of Cu, Au, Ni/Ag, and Cu/Ag alloys (with 50:50 atomic ratio) exhibit a resonant CD at $\lambda$ values of 750, 600, 500, and 480 nm, respectively. Cu nanohelices have a chiroptical red-shift of the longitudinal mode from 575 to 750 nm with an increase of $P$ from 20 to 100.
Ag nanohelices exhibit a pair of bisignate CD peaks located at 370 nm and in the visible region, which are ascribed to the transverse and longitudinal LSPR modes, respectively. The elongation of Ag nanohelices can barely shift the transverse CD mode, but cause a marked red-shift in the longitudinal CD mode.

The rotational symmetry can be effectively retained in the multi-helical NHs, which are predicted to act as broadband circular polarizers in the visible region with highly pure transmitted CPL. The right-handed triple-helical Pt NHs in a 12 × 12 array are deposited by tomographic rotatory growth combining with focused ion beam induced deposition (Figure 1.10a). Each triple-helical Pt NH has a D of 375 nm, d of 110 nm, and P of 705 nm. The distance between the centers of two adjacent single-helices is 235 nm (Figure 1.10b,c). Under a normal incidence, the transmittance and conversion spectra of the square array of triple-helical Pt NHs (Figure 1.10d, e) are monitored to show a CD as large as 37% at a wavelength of approximately 700 nm and a broadband CD in the visible-NIR region (in a wavelength range of 500 to 1000 nm), in good agreement with finite-difference time-domain (FDTD) simulation (Figure 1.10f). The losses of $T^{+}$ and $T^{-}$ are mainly due to the differential absorption (Figure 1.10a), because the reflection measurement shows very small reflectance of LCP and RCP. The triple-helical array exhibits an S/N ratio not less than 10 dB in the entire measured range (Figure 1.10g). The maximum S/N ratio is 24 dB in the wavelength range of 500 to 600 nm, two times larger than that previously reported for single-helical NHs. The triple-helices with 120° spatial arrangement have a threefold rotational symmetry and give rise to the high S/N ratio. However, the geometrical anisotropy of the single-helix allows partial transmission of the opposite light polarization (i.e., circular polarization reversion) to deteriorate the purity of the transmitted CPL.

Although these top-down fabrication methods can precisely sculpture the nanostructures with a feature size, self-assembly technology provides an alternative
bottom-up approach to synthesize building blocks into multiatom functional systems. The use of a self-assembly method with the help of natural physical or chemical forces, including Van der Waals forces, capillary forces, static forces, and electromagnetic forces, various metallic NPs with different chemical compositions, sizes, and materials can be precisely positioned and controlled. As a whole, chiral plasmonic structures with engineerable dimensions and chiroptical activity can be assembled.

**Figure 1.10** Triple-helical Pt NHs fabricated by the combination of tomographic rotatory growth and focused ion beam induced deposition. (a) Fabrication schematics. (b, c) SEM images of the NH array with different magnifications. (d) Schematic representation to indicate the handedness of incident and transmitted CPL in the experimental measurements. (e) Transmission spectra. (f) Measured (solid line) and simulated (dashed line) CD, defined as $(T^{++} - T^{-})/(T^{++} + T^{-})$. (g) Measured signal-to-noise (S/N) ratio, defined as $(I^{++}/I^{-+})$ and $(I^{--}/I^{-+})$. 47

Here in Figure 1.11a, bifacial DNA origami templates are used to generate plasmonic chiral nanostructures with four gold NPs. The rectangular DNA origami template is designed with three binding sites on the top and the fourth site on the bottom. It can be used to create LH or RH structures by setting the fourth binding sites in the LH or RH geometry. As a result, a characteristic symmetric bisignate CD spectrum is observed in the visible region. 1

The gold NPs modified with special DNA strands can bond with the DNA origami
template at predesigned positions. Because of the folding strands, the rectangular DNA template will roll up to become a 3D DNA origami tube. This DNA ‘origami’ method enables the synthesis of both LH and RH chiral metamaterials that exhibit chiroptical activity from 400 to 700 nm, as shown in Figure 1.11b. The CD spectra of the LH chiral plasmonic metamaterials and the RH chiral plasmonic metamaterials are roughly symmetric to each other. The CD spectrum can be adjusted by adding silver or silver-gold alloys to lead the plasmonic resonance to blue-shift to a shorter wavelength.49

Figure 1.11 (a) Four gold NPs assembled with bifacial DNA template in LH, RH, and achiral structures and their corresponding CD spectra.1 (d) Schematic illustration of DNA-guided self-assembly of plasmonic nanohelices with LH and RH structures and their corresponding CD spectra.49

1.1.6.3 Ultraviolet region

Biomolecules typically absorb UV light with a wavelength (λ) shorter than 250 nm; however, they usually have a sub-wavelength size that can barely perceive CPL, leading to low chiroptical activity.11 To effectively enhance the biomolecules’ chiroptical activity, amplification of an optical chirality (denoting chirality density) of CPL in the UV range12-13 has been proposed as a means of enhancing the CPL absorption of biomolecules. Numerical simulation reveals that chiral metamaterials can resonantly enhance the optical chirality of CPL in the vicinity of their surfaces at a λ value corresponding to the LSPR.14 Therefore, it causes a fundamental
demand on the production of chiral metamaterials with LSPR and chiroptical activity (i.e., resonant CD) in the UV region.\textsuperscript{15}

Noble metals typically have an engineerable LSPR and resonant CD in the visible region, but there are few reports on the fabrication of chiral metamaterials with chiroptical activity at $\lambda$ values of less than 300 nm. Aluminum (Al) is a practically promising material to generate UV-active plasmons\textsuperscript{50} due to its natural abundance on earth, its low cost, and its facile processing.\textsuperscript{51} The LSPR of AlNPs can be tailored in the UV–visible region as a function of the NP size and the percentage of Al$_2$O$_3$ in the AlNPs.\textsuperscript{52-53} Little has been reported about chiral AlNPs; in this study, the authors fabricated chiral AlNPs by asymmetric deposition of Al on the chiral shaped etch pits (Figure 1.12a). Figure 1.12e shows that the chiral AlNPs exhibit a set of bisignate CD peaks at $\lambda$ values of 250 to 700 nm (Figure 1.12e), and near-field electromagnetic simulation shows a five-fold enhancement in the optical chirality for UV and visible resonance (Figure 1.12f).\textsuperscript{54}

Al has a melting point of 660.3°C, which is markedly lower than those of noble metals, so it is difficult to sculpture Al in the helices by GLAD as a result of temperature-enhanced adatom diffusion on the as-deposited AlNPs. Magnesium (Mg) is an alternative metal that is active in the UV region. In this study, the authors propose to dope Mg with a complementary metal titanium (Ti) to accomplish a helical sculpture by GLAD by doping 8% of Ti into Mg (with a melting point of 650°C) to produce Mg nanohelices (Figure 1.13a).\textsuperscript{55} The fabricated Mg-Ti alloy nanohelices have shown extinction and CD spectra from 400 to 700 nm and are especially active in the UV region.
Figure 1.12 (a-d) Schematic for the transfer of AlNPs from a surface to an aqueous trisodium-citrate–stabilized colloid. (e) Measured and (f) simulated CD and g-factor spectra of Al chiral NP dispersion in water.  

Figure 1.13 Mg nanohelices. (a) SEM images of Mg LH (left-top panel) and RH (left-bottom panel) nanohelices. The right panel shows a top view of the array of the Mg LH nanohelices.
Biomolecules typically absorb UV light with a wavelength shorter than 300 nm, resulting in an urgent demand to produce deep UV-active plasmonic metamaterials to resonantly enhance the chiroptical response of biomolecules of interest. However, reports on this topic are limited. In my dissertation, therefore, to further apply chiral plasmonic metamaterials to enhance and detect biomolecules’ CD signals, studies on chiroptical active AlNPs will be introduced.

1.1.7 Applications of chiral plasmonic metamaterials

1.1.7.1 Circular polarizers

A helix serves as a circular polarizer; one CPL strongly interacts with a helix with a given handedness and is mostly reflected, whereas the other circular polarization is nearly completely transmitted. Metallic NHs with a sub-micrometer $P$ can function as a circular polarizer in the UV–visible–NIR range. For example, a $5 \times 5$ array of right-handed five-pitch Pt NHs with a $P$ of approximately 200 nm, deposited by focused ion beam induced deposition, is illuminated by LCP and RCP along the direction of the substrate normal, and non-polarized transmittance is monitored in a spectral range of 800 to 1300 nm. The right-handed Pt NHs strongly suppress RCP, and LCP is transmitted more than RCP in more than 30% in the NIR range of 1000 to 1300 nm. The Lumerical FDTD simulation reveals that at a wavelength of 1200 nm, the electric-field intensity $|E|$ of LCP is almost constantly guided along the helical length, accounting for the high transmission. In contrast, the $|E|$ of RCP is mainly confined on the top of the right-handed Pt NH to reduce the transmission to the subsequent loops.

Flexible engineering of helical structures by GLAD enables one to generate heterobiaxial Ag NHs that consist of one-pitch left-handed and one-pitch right-handed
NH, where there is a misalignment of the longitudinal axes of the two incorporated NHs.\textsuperscript{41} The resonant L-CD mode of the hetero-biaxial Ag NHs nearly flips around the zero-CD axis, while switching the direction of the CPL incidence from the top to the bottom of the hetero-biaxial arrays. It is illuminated that the hetero-biaxial Ag NHs can function as a circular polarizer in the visible region, triggered simply by rotating the hetero-biaxial arrays under a given optical incidence. Intriguingly, when the two longitudinal axes are aligned, that is, the hetero-coaxial Ag NHs, the function of the visible circular polarizers caused by switching the incident direction is eliminated. It is indicated that such a function of visible circular polarizers originates mainly from hetero-biaxial misalignment.

\textbf{1.1.7.2 Broadband light absorption}

Diverse photoconversion processes, such as solar cells and photocatalytic hydrogen generation, essentially demand broadband light absorption. A close-packed random array of Ag NHs coated with $\alpha$-Fe$_2$O$_3$ (hematite) NPs shows broadband enhancement of light absorption in a wavelength range of 400 to 1000 nm.\textsuperscript{57} Compared to the visible-NIR absorption of a thin film made from hematite NPs, the regular Ag NHs with a given $D$ have an absorption enhancement of 45\%, and the conical Ag NHs that contain a $D$ gradually increase with the growth of Ag NHs with absorption enhancement of 52\%. The broadband enhancement of light absorption can be attributed to the LSPR of the Ag NHs and the enhanced optical absorption of hematite NPs due to the strong near fields of the Ag NHs. Another example is the close-packed random array of two-pitch NHs, composed of one-pitch Al NH on top and one-pitch Ag NH at the bottom.\textsuperscript{58} The pitches of Ag and Al NHs are 183 and 265 nm, respectively. The hybrid NH arrays exhibit polarization-independent, broadband (in a wavelength range of 400 to 2000 nm), omnidirectional (in a range of angles of incidence from 0° to 70°) extinction over 90\% in average. The densely packed array has a small NH-to-NH gap that is
comparable to or less than the helical size that strongly amplifies LSPR at the gaps. FDTD simulation reveals that the electric field is strongly localized in the narrow, dielectric regions between the top and bottom NHs, accounting for the broadband, omnidirectional light trapping and absorption.

1.1.7.3 Refractive index sensing

LSPR-based sensors typically operate by monitoring a shift of the resonance absorption peak in response to a change of $n$, the refractive index of the local medium surrounding plasmonic NPs. The resonant CD signal of plasmonic NHs is usually bipolar, and the CD crossing point (the wavelength of $\lambda_0$ at which CD is equal to zero; Figure 1.14a) corresponds to the peak position in the plasmonic extinction spectrum. $\lambda_0$ in the resonant CD spectrum can serve as a natural point for tracking, better than tracking the peak position of the plasmonic extinction peak that rarely appears sharp. CD offers an alternative to the extinction-based refractive index sensing, by tracking the shift of $\lambda_0$ in response to changes in $n$. The refractive index sensitivity $S_n$ is defined by

$$S_n = \frac{d\lambda_0}{dn} = \frac{-2\tilde{\chi}n(\lambda_0)}{(d\varepsilon_r/d\lambda)\lambda_0} \quad (1.11)$$

where $\tilde{\chi}$ is the shape-dependent factor, and $\varepsilon_r$ is the real part of the dielectric function of the plasmonic material. Practically, it tracks the shift of $\lambda_0$ in response to the volume concentration $c$ of the species of interest, given by

$$\frac{d\lambda_0}{dc} = \frac{d\lambda_0}{dn} \frac{dn}{dc} = S_n[n_2(\lambda_0) - n_1(\lambda_0)] \quad (1.12)$$

where $n$ of a mixture of a solute (with refractive index of $n_2$) in a solvent (with refractive index of $n_1$) is approximated as

$$n = n_2c + n_1(1 - c) \quad (1.13)$$
Figure 1.14 Highly sensitive refractive index sensors: (a-c) left-handed Mg NHs; (d) left-handed Ag:Ti alloy NHs. CD spectra of Mg NHs in a DMSO-water mixture with a volume concentration ($c$) of DMSO in a range of 0% to 30%: (a) over the full spectral range; (b) in partial spectral range at $\lambda_{01}$ (left panel) and $\lambda_{02}$ (right panel). (c) Wavelength shift of $\lambda_{01}$ and $\lambda_{02}$, relative to water, as a function of $c$. (d) Left and right panels show the effects of helical height and Ti composition, respectively, on diverse sensing parameters.

In a water ($n_1$)-DMSO (dimethyl sulfoxide, $n_2$) system, the differential $n$ (i.e., $n_2 - n_1$) is greater in the UV range (at $\lambda_{01}$, which is 0.229 RIU at 250 nm) than that in the visible region (at $\lambda_{02}$, which is 0.144 RIU at 600 nm), and UV-enhanced sensing is demonstrated by Mg NHs that have UV-active LSPR (Figure 1.14). The shift of $\lambda_{01}$ (at approximately 260 nm) is greater than that of $\lambda_{02}$ (at approximately 550 nm) (Figure 1.14b), and the detection sensitivity in the UV region is greater than that in the visible region (Figure 1.14c), in agreement with the finding that the differential $n$ in the UV range is 1.6 times larger than that in the visible region. It is clearly illuminated that chiroptically active UV plasmonics are promising for high $n$-associated sensitivity due to the medium’s dispersion.
Eq. 1.11 indicates that an elongation of NHs (in terms of $\chi$) and a decrease in the $\varepsilon_r$ dispersion are favored to raise $S_n$. The material dispersion function can be flattened by alloying a plasmonic material (e.g., Ag) with a weakly dispersive metal (e.g., Ti) to yield a negative, but flatter $\varepsilon_r$. Co-deposition GLAD of Ag and Ti is performed to deposit Ag:Ti alloy NHs with two pitches, atomic ratios of Ti between 3% and 23%, and helical heights ($H$) between 113 and 157 nm. In conjunction with the sensitivity $S_n$, it is also important to consider the accuracy with which a spectral feature can be resolved, by evaluating the full width at half maximum (FWHM) and figure of merit (FOM) of a spectral peak given by

$$\text{FWHM} = \frac{4\sigma \varepsilon_i^2}{|\delta\chi\varepsilon_r^2(\alpha_{er})|}$$ (1.14)

$$\text{FOM} = \frac{S_n}{\text{FWHM}} = \frac{1}{2\sigma \varepsilon_i^2}$$ (1.15)

where $\sigma$ is the instrumental resolution, and $\delta\chi$ describes the shape factor that depends on the particle chirality. The left column of Figure 1.12d shows that the elongation of Ag$_{0.97}$Ti$_{0.03}$ NHs (i.e., an increase of $\chi$) causes an increase of $S_n$ (eq. 1.11), but the FWHM remains unchanged owing to the independence of FWHM on $\chi$ (eq. 1.14), so that the FOM increases dramatically. The Ag$_{0.97}$Ti$_{0.03}$ NHs with an $H$ of 157 nm exhibit FOMs of 2,859 RIU$^{-1}$. The right column of Figure 1.14d illustrates the effect of engineering the dispersion function of $\varepsilon_r$ via doping of Ti. Flattening the material dispersion function gives rise to an increase in $S_n$ and FWHM, according to Eqs. 1.11 and 1.14. The net effect causes the FOM to reach a maximum value at an intermediate doping of 11% Ti. The high $n$-sensitive Ag:Ti NHs are used to detect avidin-binding on biotin. For the Ag$_{0.97}$Ti$_{0.03}$ NHs with an $H$ of 113 nm, the avidin-binding causes $\lambda_0$ to redshift by $\sim$3 nm, and the rise time is approximately 5 min. The Ag$_{0.89}$Ti$_{0.11}$ NHs with the same $H$ show a stronger response with a greater $\lambda_0$ shift of 5 nm, and the enhancement of the sensitivity is attributed to the reduced dispersion.
1.1.7.4 Nanorheological measurement

Alloying of plasmonic and magnetic materials in metallic NHs leads to a distinct chiroptical activity that varies in a sensitive manner with the NHs’ orientation with respect to the propagation direction of the incident CPL (i.e., wave vector $k$ of the incident CPL; Figure 1.15a). Co-deposition GLAD gives rise to the generation of two-pitch NHs made of Au:Fe alloys with a 1:1.5 atomic ratio that have an $H$ of approximately 170 nm (Figure 1.15e). The Au:Fe NHs exhibit ferromagnetic behavior and have a coercive field of 29.5 mT and a remanence ($m_r$) of $1.2 \times 10^{-14}$ emu per helix. The weakly ferromagnetic NHs have magnetic anisotropy, and an application of an external field gives rise to an alignment in which the magnetic moment $m$ of a ferromagnetic NH, and hence its body, lies parallel to the magnetic field $B$ in a static regime (Figure 1.15a). The chiroptical response of the dispersed ferromagnetic NHs is as a function of $\theta_B$ (an angle between $k$ and $B$; Figure 1.15d). A variation of $\theta_B$ from 0° to 90° causes a flip of the CD spectrum around the zero-CD axis in sign (Figure 1.15a), and rotation of $B$ with respect to $k$ shows symmetric modulation of the CD signals (Figure 1.15b). In response to a magnetic field rotating at frequency $f_B$, a magneto-plasmonic NH will rotate at an angular frequency $\omega$ in a complex fluid environment (Figure 1.15c, d). Viscous drag will cause a phase lag $\phi$, an angle between $B$ and $m$, given by

$$\sin \phi = \frac{2\pi \bar{X}}{m_r B} \eta f_B$$ (1.16)

where $\eta$ is the local viscosity of the fluid. The rotating $B$-modulated chiroptical signal can be used to extract $\phi$ for a nanorheological evaluation of $\eta$. Blood is a practically challenging test case because it strongly absorbs light, but the measurement of differential extinction (i.e., CD) of the magneto-plasmonic NHs dispersed in the blood (Figure 1.15f) can be performed for sensitive evaluation of the blood viscosity. The nanorheological measurement reveals that the blood has a
low viscosity, almost independent of the concentration of hematocrit in the blood (Figure 1.15g). However, macrorheological measurements show that the blood has an $\eta$ with a roughly linear increase and a rising hematocrit concentration. The difference is because macroscopic rheometry measures the complex viscoelastic contribution of the hematocrit in the blood, whereas only the nanoscale viscosity of the interstitial blood is evaluated sensitively by the ferromagnetic NHs. Therefore, the nanorheological measurement represents a novel approach to observe the blood plasma viscosity, which is an important indicator in diverse blood-related diagnoses that does not require separation of blood cells from whole blood before diagnosis.

1.1.7.5 Magnetic nanopropellers

Remote actuation of a magnetic NH to move to a specific location in vivo is driven largely by biomedical applications. A rotating magnetic field is applied to remotely navigate the directional motion of Ni:Pd NHs, fabricated by template-assisted electrosynthesis. The Ni:Pd NHs display a propulsion behavior of a tumbling motion at low magnetic rotation frequencies ($f_B$) and a corkscrew motion at high $f_B$, which is in good agreement with the theoretical prediction. At a high $f_B$ of 150 Hz, an Ni:Pd NH with a $D$ of 400 nm and $H$ of 3 μm corkscrews in a water droplet over a long path of approximately 45 μm parallel to the rotating magnetic field axis within a period of 3 s. Accordingly, the propulsion speed is 15 μm/s, corresponding to a relative speed of approximately 5 body lengths per second. The propulsion speed has a nearly linear increase with $f_B$, and large Ni:Pd NHs with a $D$ of 400 nm corkscrew nearly three times faster than small NHs with a $D$ of 100 nm. The Ni:Pd NHs can also be remotely actuated to propel in cell culture media.
Figure 1.15 Nanorheological measurement using magneto-plasmonic Au:Fe NHs. (a) Principle of magnetically driven chiroptical switching. Engineering the alignment of external magnetic field $\mathbf{B}$ (and the longitudinal axis of an Au:Fe NH) and the wave vector $\mathbf{k}$ of the incident CPL leads to modulation of the CD signals of the dispersed NHs. (b) CD responses of the dispersed NHs under a static $\mathbf{B}$ of 1 mT in a wavelength range of 230 to 1100 nm at an angular interval of 45°. Dark-field images of a single NH (scale bar: 1 μm) are snapshots taken during continuous in-plane rotation. (c) Schematic of Au:Fe NHs dispersed in a complex and optically dense medium, that is, blood plasma surrounded by erythrocytes. (d) Definition of the angles and parameters used in the nanorheological measurement ($\mathbf{m}$: magnetic moment along the longitudinal axis of the NH; $\phi$: phase lag between $\mathbf{B}$ and $\mathbf{m}$; $\theta_{B}$: angle between $\mathbf{B}$ and $\mathbf{k}$; $\theta_{m}$: angle between $\mathbf{m}$ and $\mathbf{k}$; $\omega$: angular velocity of rotating NH. (e) Scanning TEM image and EDX false-color elemental map of a two-pitch Au:Fe NH. (f) Extinction and CD spectra of the Au:Fe NHs dispersed in bovine blood plasma surrounded by the erythrocytes at different volume fractions. (g) The measured dynamic viscosity $\eta$ of the bovine blood plasma in the presence of red blood cells with different hematocrit levels. For comparison, the macroscopic measurement is made at shear rates $\gamma$ of 2.4 s$^{-1}$ and 49.2 s$^{-1}$.

Many biological media contain dense gel-like networks of interconnected polymer chains with mesh sizes in a range of tens to hundreds of nanometers. GLAD is used to generate SiO$_2$ NHs (with a $P$ of 100 nm, $d$ of ~70 nm, $D$ of 120 nm, and $L$ of 400 nm) and microhelices (with a $D$ of 450 nm and $L$ of 2.5 μm) that contain a 40-nm-thick Ni-segment. Remotely actuated by a strong magnetic field of 100 Oe above the coercive field of 65 Oe, the Ni-contained SiO$_2$ NHs display propulsion velocities and dimensionless velocities (the propulsion velocity normalized by $P$...
and $f_{\text{h}}$) greater than those of the microhelices in viscoelastic hyaluronan solutions.\textsuperscript{65} The gel mesh has a size comparable to that of the SiO$_2$ NHs but much smaller than the microhelices, which can be ascribed to the steric effect. The optimal length is about one helical pitch, resulting from a trade-off between maximization of the net chirality and minimization of the rotational viscous friction of the helical nanopropellers.\textsuperscript{66} The SiO$_2$ NHs show significantly enhanced propulsion velocities that exceed the highest measured speed in Newtonian fluids.

**1.1.8 Photocatalytically asymmetric syntheses**

The generation and manipulation of molecular chirality undoubtedly ranks among the most important topics in modern chemistry. A pair of enantiomeric compounds, as mutual non-superimposable mirror reflections, are known to have essentially the same generation free energy from prochiral precursors and should commonly be formed with equal probability. Practically, most artificial enantiomeric enrichment and purification is obtained by enantiodifferentiating reactions or resolutions mediated by chiral molecules. Several intriguing chiral phenomena, such as spontaneous symmetry breaking,\textsuperscript{67} chirality amplification, and asymmetric autocatalysis,\textsuperscript{68} are relevant to this issue. Efforts have been devoted to explore the external physical factors, including CPL\textsuperscript{69} and magnetic field,\textsuperscript{70} to obtain enantiomeric enrichment in the absence of any chiral matter.\textsuperscript{71}

Early in the 1970s, research workers found that CPL can be used to catalyze asymmetric syntheses; however, the enantiomeric excess (ee) of products was less than 5%.\textsuperscript{72-73} In 1997, it was reported that intense CPL from an XeF (351 nm) excimer laser could induce enantioenrichment, which increases the ee to 10%.\textsuperscript{74} These experimental results inspired researchers to work on manipulating the CPL to catalyze asymmetric syntheses.
In 2004, Soal et al.\textsuperscript{75-76} used CPL mediated with a chiral olefin for asymmetric synthesis to achieve an $ee$ above 90\% in Figure 1.16. Although it is of fundamental and practical significance to manipulate the CPL to catalyze asymmetric syntheses of, for example, single-enantiomer drugs without negative or even fatal side effects; however, the amplification of near-field optical chirality induced by the plasmonic NHs paves the way to achieve such an objective. Macroscopic chiral operations, such as vortex and stirring,\textsuperscript{77} have demonstrated the ability to generate chirality of supramolecular aggregates. However, to manipulate molecular chirality through such operations is evidently challenging because it demands a chirality transfer of visible macroscopic behavior to a size as small as sub-nanometer. In my work, I use macroscopic rotation of a substrate holder to control the handedness of PhNPs and mediate the enantioselective photocyclodimerization of AC.

### 1.2 Mesoporous SiNWs (mp-SiNWs)

#### 1.2.1 Background of SiNWs

Nanomaterials, which cover vast research fields, including physics, chemistry, materials science, and biology, have attracted great interest in recent years. Among diverse studied nanoscale structures, one-dimensional (1D) SiNWs have been
recognized as promising candidates and have seen rapid development for several reasons. First, silicon is the second abundant element in the world. Second, silicon is a semiconductive material that is compatible with most processing techniques. Last, SiNWs with unique chemical, optical, electronic, and optoelectronic properties have been intensively investigated for their fundamental properties and wide range of potential applications. Recently, increasing attention has been paid to mesoporous SiNWs (mp-SiNWs); it was reported in 2009 that SiNWs were electrochemically porosified to create mp-SiNWs.

Structural porosification has promoted the application of mp-SiNWs in energy storage, batteries, photocatalysis, and drug delivery. Taking photocatalysis for an example, mp-SiNWs have been regarded as potential candidates because of their abundant pores, increased surface area of the porous profile, and ease of recycling compared with nanopowders. MACE has generally been used to create mp-SiNWs in a simple, inexpensive way; the fabrication technique and mechanism are presented in next section. Mp-SiNWs have emerged in the past decade as a novel 1D structure, and there is still an urgent need to determine how to conveniently engineer the porosity and functionalize the surface morphology for multiple applications.

1.2.2 MACE

mp-SiNWs are produced by MACE of Si wafers, an anisotropic, galvanic etching. MACE is classified as one-step MACE (1-MACE) and two-step MACE (2-MACE); in my work, I focus mainly on 1-MACE, which involves a series of (electro)chemical reactions, given by

\[ Ag^+ + e^- \rightarrow Ag(s) \quad (E^0 = 0.80 \text{ V}) \quad (1.17) \]
\[ Si(s) + 2H_2O - 4e^- \rightarrow SiO_2(s) + 4H^+ \quad (E^0 = -0.84 \text{ V}) \quad (1.18) \]
\[ SiO_2(s) + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (\Delta H = -(138.22\pm1.36) \text{ KJ/mol}) \quad (1.19) \]
The redox potential $E$ is versus standard hydrogen electrode (SHE). $\Delta H$ is the reaction enthalpy, and the negative sign illustrates that a reaction generates heat.

**Figure 1.17** (a) Quasi-quantitative energy diagram at the silicon-electrolyte interface at the beginning of 1-MACE of n$^{++}$-Si(100). The energy is referred to standard hydrogen electrode (SHE) potential. Heavily doped n-Si has Fermi energy ($E_F$), valence and conduction band in the bulk ($E_{VB}$ and $E_{CB}$) and at the interface ($E_{VB,S}$ and $E_{CB,S}$), and space charge layer (SCL) with width $W_{SCL}$. $\Delta \Phi$ is an energy barrier between $E_F$ and $E_{CB,S}$. $E_{Ag+/Ag}$, $E_{Ag}$ represent the potential energy of the redox pair, Ag$^+$ and Ag in the electrolyte, respectively. $\lambda$ is the reorientation energy. The light blue sphere represents an electron at $E_F$, and the I-IV processes denote a series of electron migration from the bulk to the interface. (b) Energy diagram with a variation of doping levels in n-Si(100). (c) Schematic of 1-MACE evolution. For clarity, only one non-grown Ag nucleus is shown scratching the wafer in the mpSi, marked by a red dashed line. Within a period of time $\Delta t$, the evolution of the porosification and mp-SiNWs are denoted by $\Delta T_P$ and $\Delta T_{NW}$, respectively. 78

1-MACE is generally performed in an aqueous solution containing hydrogen fluoride (HF) and AgNO$_3$, 79 involving the nucleation of Ag NPs and scratching (or sinking) of the growing NPs into the bulky Si wafers. 80 Ag$^+$ ions near the wafer capture electrons (eq. 1.17) that are donated by the anodic oxidation of Si (eq. 1.18) and nucleate on the wafer surface. Ag nucleation is thermodynamically ascribed to Ag’s slightly higher electronegativity than Si. HF dissolves the oxidized SiO$_2$ (eq. 1.19) to create pits that trap the Ag nuclei. Ag NPs preferentially adhere to surface states, such as dangling bonds, structural defects (steps, kink sites, and
dislocations), and sites around the dopants. The oxidation of one Si atom generates four electrons (eq. 1.18), and the reduction of an Ag$^+$ ion consumes only one electron (eq. 1.17). The excess electrons donated from the wafer migrate to and accumulate on the surfaces of Ag NPs and electrostatically drive Ag$^+$ ions to diffuse toward the nuclei for reduction. Because of the abundant substances in the electrolyte and wafer, eq. 1.17-1.19 can repeatedly take place. As a result, Ag NPs continuously scratch and sink into the wafer and simultaneously grow into dendrites. The residual of the scratched wafer appears to be an array of SiNWs without pores, which retain the intrinsic electronic properties of the parent wafer. The scratching of Ag NPs is prohibited along the lateral direction perpendicular to the substrate normal, because the etching rate determined by the curvature of a pore reaches the minimum along the lateral direction. The sinking direction of the growing NPs governs the surface crystalline orientation of the as-generated SiNWs and is comprehensively determined by the crystalline structure of parent wafers, etching temperature and duration, and electrolyte concentration.

Solid SiNWs are usually created by 1-MACE of lightly and medially doped wafers, and the porosification of SiNWs is triggered by increasing the wafers’ doping level. For instance, 1-MACE of n$^{++}$-Si(100) creates mp-SiNWs. The heavy doping-induced porosification can be understood by a thermodynamic model that describes charge transport across the silicon-electrolyte interface driven by potential energy (Figure 1.17a). Eqs. 1.17 and 1.18 simply address the electron transport from Si to Ag$^+$ ions, which is composed of processes I-IV at the Si/electrolyte interface. Electrons at $E_F$ of Si wafers migrate to the interface by overcoming a potential energy barrier $\Delta \Phi$, consisting of the excitation barrier ($E_{CB}$-$E_F$, the process I) and the band edge bending in SCL ($E_{CB,S}$-$E_{CB}$, the process II). Owing to the mismatch of $E_{CB,S}$ with $E_{Ag^+}$, electrons are apt to relax to surface states ($E_{SS}$) aligned with $E_{Ag^+}$ (the process III) followed by the resonant migration to $E_{Ag^+}$ (the process IV). The increase in the doping level not only upshifts $E_F$ toward $E_{CB}$ to reduce $\Delta \Phi$, but also
makes the SCL thinner to promote electron tunneling through the SCL (Figure
1.17b), to facilitate processes I and II. Hence, a large amount of Ag$^+$ ions nucleate
on the surface, and [Ag$^+$] (i.e., the concentration of Ag$^+$ ions) is significantly
reduced in the electrolyte. A low [Ag$^+$] can support only a portion of Ag nuclei to
grow and scratch the bulk Si. The remaining non-grown Ag nuclei will undergo
random scratching in a short period of time to porosify SiNWs and the bulky wafer
(Figure 1.17c). Because the scratching of growing Ag NPs is limited by the
diffusion of Ag$^+$ ions with low [Ag$^+$], the random porosification tends to be faster
than the NP scratching. Consequently, the electrochemical porosification tends to
generate a hybrid structure composed of an array of mp-SiNWs on mpSi (Figure
1.18a-d). In contrast, the light and medial doping increases $\Delta \Phi$ to prevent Ag$^+$ ions
from severe consumption. High [Ag$^+$] substantially supports that notion that most
Ag NPs grow and scratch the wafer to create SiNW and effectively suppress
porosification (Figure 1.18e, f). This model can also account for the creation of mp-
SiNWs via 1-MACE of p++-Si.$^{87}$

To promote the porosification in 1-MACE of n+-Si, processes I and II are thermally
excited by raising the etching temperature from room temperature to 60°C and
increasing the HF from 2.4 to 5 mol/L.$^{88}$ The dissolution of SiO$_2$ by HF is a heat-
releasing reaction with negative enthalpy (eq. 1.19), and the generated heat
increases thermodynamically with HF. The thermal promotion of electron
migration across the interfaces contributes to the fabrication of n$^+$-mp-SiNWs
(Figure 1.19a) with the porosity gradually decreasing from the tops to roots (Figure
1.19b-d), and there is a lack of mpSi underneath (Figure 1.19d). Compared to 1-
MACE of n$^{+2}$-Si, thermal excitation in 1-MACE of n$^+$-Si generates less non-grown
NPs, and thus the porosification of non-grown Ag NPs occurs more slowly than the
scratching of growing Ag NPs, which accounts for the generation of the gradient
porous structures without mpSi (Figure 1.20).
Figure 1.18 1-MACE of n^{++}-Si(100) generates mp-SiNWs and a layer of porous Si (mpSi) underneath (a-d), and that of n^-Si(100) (e) and n'^-Si(100) (f) creates SiNWs without mpSi. (a, b): TEM images; (c): SEM cross-sectional view; (d-f): SEM oblique views.87

Figure 1.19 (a) SEM image of n'^-mp-SiNWs. (b-d) High-magnification SEM images of portions (I), (II), and (III) in (a).88

The doping level and the electronegativity of dopants both play significant roles in electrochemical etching. For example, the dopants of n-Si include P with an electronegativity of 2.19, As of 2.18, and Sb of 2.05 and function as the surface states ($E_{SS}$). In 1-MACE of n'^-Si, doping with Sb can generate SiNWs,86 but the
As-doping fails. It is illuminated that the dopants preferentially have small electronegativity for promoting process IV. With respect to n\textsuperscript{++}-Si, the accumulation of a large amount of electrons in the vicinity of dopants overbalances the high electronegativity of As, so as to facilitate process IV and create n\textsuperscript{++}-mp-SiNWs via 1-MACE of As-doped n\textsuperscript{++}-Si. In terms of n\textsuperscript{-}Si, the surface defects mainly serve as the surface states instead of the dopants that have a relatively low concentration, to decouple the dopant electronegativity with the generation of SiNWs. Therefore, SiNWs can be fabricated by MACE of P-doped n\textsuperscript{-}Si. The background of MACE is partially reproduced from *JSM Nanotechnol Nanomed* 3(1): 1035.

![Figure 1.20](image)

Figure 1.20 (a) SEM cross-sectional image of n\textsuperscript{-}-mp-SiNWs with a trapezoid structure. (b, c) Schematic illustrations of the generation of trapezoid n\textsuperscript{-}-mp-SiNWs via 2-MACE of n\textsuperscript{-}-Si.

1.2.3 Applications of mp-SiNWs

Derived from structural porosification, the enhanced surface-to-volume ratio generates enormous voids for mass storage and transportation that have been developed for a wide range of applications in energy storage, drug delivery, gas sensors, and PL.
1.2.3.1 Energy storage

The use of SiNWs as an anode in lithium ion batteries has been extensively investigated recently because of their strain toleration and high surface area, which can better accommodate the large mechanical strain. In 2008, Peng et al. first used SiNWs fabricated by MACE as an anode for lithium ion batteries. They found that the good conductivity and rough surface of SiNWs would lead to good charge capacity and long cycling performance. However, the residual silicon wafer would deteriorate the anode’s capacity. In this situation, Huang et al. coated carbon and aluminum films on the SiNWs to improve the lithium storage capacity, charge and discharge cycling performance, and Coulombic efficiency. Similarly, Qiu et al. coated NiO on SiNW electrodes to achieve better lithium storage capacity and cycling stability.

1.2.3.2 Sensors

Because of their distinct advantages, such as a high surface area and unique charge transport properties, SiNWs have been investigated for potential applications in chemical and biological sensors. In particular, surface-enhanced Raman scattering (SERS) for biosensors based on SiNWs have been investigated. Traditional SERS-active materials are silver or gold NPs, and researchers have recently worked on the use of SiNWs as a SERS substrate to combine large-area nanostructures with nanogaps less than 10 nm. Qiu et al. fabricated closely spaced Ag-capped SiNWs to investigate SERS. They found large SERS intensity for shorter SiNWs and smaller signals for longer SiNWs, which can be explained by the agglomeration of Ag caps and the bending of longer SiNWs. However, the random spacing and lack of uniformity among individual nanowires would destroy the reproducibility of the SERS signal. Huang et al. coated Ag on the surface of hexagonally packed SiNWs (Figure 1.21c) to achieve ultrasensitive single-molecule detection and used interparticle nanogaps as hot spots in SERS to detect long double-stranded
DNA with 14% relative standard deviation for more than 4000 spot measurements. The authors ascribed such high reproducibility to the long distance between the SiNWs and the coated Ag, where the surface plasmon can propagate along the continuous Ag layer.

Figure 1.21 (a) SERS spectra of pure 4-aminothiophenol (4-ABT), Rhodamine 6G (R6G), 1,2-di(4-pyridyl)ethylene (BPE), and their trianalyte mixture from AgNP/SiNWs array. (b) Salmon dsDNA SERS spectra from Ag/SiNW arrays and silver film on nanospheres (AgFON), respectively. Spectra are shifted vertically for clarity. (c) SEM image of ∼20-nm Ag film-coated SiNWs 110 nm in diameter and ∼700 nm long. Inset: TEM image shows that the Ag film was continuous. Scale bars: 200 nm. 97

1.2.3.3 Photoluminescence

Photoluminescence originates from the radiative recombination of excitons, and the emission wavelength of PL is determined by the energy difference of two density states between which the radiative recombination occurs.98 The PL characteristics of mp-SiNWs (i.e., the intensity, the peak position $\lambda_{PL}$, the and decay time) are very sensitive to the doping level,99 porosity, and dangling bonds at the surfaces.100

The different doping levels of the bulk silicon water lead to SiNWs with variable porosity through the electrochemical etching process,101 which accounts for the blue shift of the PL spectrum from Figure 1.22a to 1.22c. The overlapping of fluorescence images with microscopic images confirms that the fluorescence originated from porous SiNWs structures.
Figure 1.22 PL spectrum of porous silicon nanowires fabricated from (a) highly doped p-type Si(100); (b) medially doped n-type Si(100) wafer; and (c) lightly doped n-type Si(100) wafer. (d, e) Overlapping between confocal PL images and microscopy images for the samples in (a, b). Even with the same doping level of bulk silicon wafer, the porosity of SiNWs would increase as a function of the etching time in oxidant H₂O₂, which leads to an effectively enhanced intensity of PL in Figure 1.23.

Figure 1.23 Porous SiNWs etched in the presence of 0.3-M H₂O₂ for 30, 60, 90, 120, and 180 min after HF treatment for samples 1 through 5, respectively.

Many studies have focused on the fundamental understanding of light emission of mp-SiNWs. Although various mechanisms about the PL of mp-SiNWs include quantum confinement, surface states, or defects in SiOₓ, the origin of light emission is still under debate.
However, from the mechanism discussion, it can be seen that PL can be engineered by surface modification of mp-SiNWs. Sun et al. studied the effects of surface passivation on the PL of SiNWs\textsuperscript{105} and found that twice the PL intensity is required to passivate the silicon surface with oxygen using an aqueous HNO\textsubscript{3} solution than with the silver/hydrogen–passivated SiNWs. Zhang et al. reported that the PL intensity increased as the porosity increased and that the Si-O bonds on the surface of the SiNWs and the oxidation of SiNWs leads to a red-shift of the PL peak.\textsuperscript{106} They considered that the origin of strong emissions was the localized state associated with Si-O bonds and mesoporous structure. Choi et al. used a focused green laser to fast-scan an array of n\textsuperscript{++}-mp-SiNWs and generated a broad greenish-blue PL spectrum centered at approximately 550 nm.\textsuperscript{107} When p\textsuperscript{'}-mp-SiNWs are conformally coated with 6 to 10 nm of polycrystalline SnO\textsubscript{2} by atomic layer deposition, the PL appears to have a slight red-shift from 510 to 530 nm.\textsuperscript{108} By annealing the SnO\textsubscript{2}-coated p\textsuperscript{'}-mp-SiNWs in N\textsubscript{2}/H\textsubscript{2} at 600°C, SnO\textsubscript{2} is chemically decomposed into Sn, which diffuses into the Si skeletons to enhance the PL (Figure 1.24).

![Figure 1.24](image-url)  
**Figure 1.24** PL spectra of SnO\textsubscript{2}-coated porous SiNWs annealed at 650°C for 30 min in various atmospheres along with the as-synthesized SnO\textsubscript{2}-coated and uncoated porous SiNWs.\textsuperscript{108}
1.2.3.4 Antireflection properties

SiNW arrays can effectively trap light to promote the photon-to-electron conversion while hybridizing with organic polymers.109-111

MACE generates an array of vertical mp-SiNWs on an Si wafer, which functions as an antireflection coating to effectively reduce the reflection loss of smooth wafers and magnify the photovoltaic efficiency of Si-based solar cells.112 The contribution of antireflection lies in two factors. First, the incident light will be multiply reflected among the close-packed vertical NWs to prevent light from escaping (i.e., optical trapping).113 Second, an antireflection coating has an index of refraction to reduce the mismatch between the air and the Si wafer. It is highly desirable for antireflection to have a tapered structure, in which the volume fraction of Si is gradually reduced from the wafer surface to the air.114 Compared to the high reflectance of bare Si wafers in the range of 80% to 36% in the UV–visible spectrum, n'-SiNWs reduce the reflectance to 2.5% to 5.5%, mainly due to light trapping (Figure 1.25a).103

![Figure 1.25](image)

Figure 1.25 (a) Reflective spectra of n'-SiNWs and n'-mp-SiNWs. n'-mp-SiNWs were created by electrochemical porosification of n'-SiNWs as function of porosification duration in the range of 1 to 3 min. (b) Magnified view of (a) in the low reflective spectra. (c) TEM image of n'-mpSiNW.103

The electrochemical porosification of n'-SiNWs can further reduce reflectance and increase the porosity (Figure 1.25b) because of the decrease in the refraction index and the increase in surface roughness (Figure 1.25c). However, To et al. used an integrated sphere to measure scattering and transmittance and found that an array
of n++-mp-SiNWs trap less light and scatter more light than n++-SiNWs with the same thickness. This porosification-enhanced light scattering may originate from the surface roughening induced by the porosification. Therefore, the enhanced antireflection with the porosity of n+-mp-SiNWs (Figure 1.25b) is more likely attributable to the tapered structures (Figure 1.25c). Charrier et al. created n+-mp-SiNWs that have not only a tapered profile (Figure 1.26a), but also a porosity that gradually reduces from the top to the root portions (Figure 1.26b). The gradient-porosity structures give rise to a graded decrease in the refraction index from the Si wafer to the air, resulting in specular reflectance of less than 0.1% in the UV–visible spectrum at an incident angle of 6 degrees (Figure 1.26b). The elongation of tapered n+-mp-SiNWs can further reduce the reflection loss owing to the enhancement of optical trapping (Figure 1.26c).

Therefore, it is of fundamental significance to engineer the optical properties to optimize the functional performances of SiNW-based light-emitting devices. Hence, in this dissertation, multiple methods, such as engineering the porosity, passivating the surface of mp-SiNWs, and surface modification with molecules, were introduced to investigate the PL and antireflection of mp-SiNWs.
1.3 Dissertation Outline

In Chapter 2, the fabrication methods of PhNPs and SiNWs are introduced, and the details of characterizations used in this dissertation are described.

In Chapter 3, neglecting the geometric limit of helices, I present GLAD with fast substrate rotation to generate helical silver NPs (AgNPs) with $P < d$ and chiroptically active in the UV–visible region. The nominal $P$ can be minimized as small as 3.5 nm, where AgNPs still have a reliable and detectable chiroptical response.

In Chapter 4, I use two GLAD-related methods, fast substrate rotation and chiroptical activity transfer, to produce chiral Al nanostructures that exhibit strong chiroptical activity in the deep UV–visible region, which has significance for further investigation of the interaction between chiral plasmonics and biomolecules.

In Chapter 5, helical AgNPs are used to mediate an asymmetric synthesis, photochirogenic cyclodimerization of 2-anthracenecarboxylate (AC).

In Chapter 6, Metal-assisted chemical etching (MACE) is carried out to generate mesoporous SiNWs (mp-SiNWs) with mesopores from 2 to 50 nm. PL and reflection loss are engineered by a new method to use a simple tape to reduce the porosity of mp-SiNWs without changes in the MACE conditions.

In Chapter 7, 40% NH$_4$F is found to etch mp-SiNWs attributed to surface F- termination caused by the nucleophilic attack of F$^-$ anions to Si atoms. It has been systematically studied the NH$_4$F-etching rate as a function of the doping levels of SiNWs, surface crystalline orientations, and porosity.

In Chapter 8, At a modest temperature of 110°C, 1,4-diethynylbenzene (DEBZ) is grafted via monosilylation grafted on H-terminated mp-SiNWs which opening a
door to flexible engineering of PL of mp-SiNWs for optoelectronic and bio-detection applications.
Chapter 2 Experimental Methods and Characterization

In this dissertation, two kinds of nanostructures are fabricated. The fabrication technique and experimental methods of generating PhNPs and mp-SiNWs are introduced in this chapter.

2.1 Plasmonic helical nanoparticles (PhNPs)

2.1.1 GLAD of PhNPs

The PhNPs with helicity were generated in this study with a custom-built physical vapor deposition system (JunSun Tech Co. Ltd., Taiwan) with a high vacuum of $10^{-7}$ to $10^{-6}$ Torr. Metals were evaporated at approximately 0.3 nm/s as monitored by a quartz crystal microbalance, using an electron-beam accelerating voltage of 8.0 kV and controlling the emission current at 15 to 25 mA for Ag (99.99%, Kurt J. Lesker), 35 to 45 mA for Al (99.99%, Torsh Technology Limited), and 30 to 40 mA for Cu (99.9999%, Torsh Technology Limited). At a deposition angle ($\alpha$) of 86 degrees with respect to the direction normal to the substrate, the metals were deposited on sapphire (MTL Hong Kong) and Si wafer (Semiconductor Wafer, Inc.) over an area of $1.5 \times 1.5$ cm$^2$ with and without surface pre-patterning.

![Figure 2.1](image.png)

**Figure. 2.1** (a) Schematic of GLAD process. The vapor from the PVD source evaporated to the substrate, whose deposition angle ($\alpha$) is greater than 75°. (b) GLAD-induced ballistic shadowing of the random adatoms. The subsequent flux are deposited onto the nuclei instead of the shadowed region.\(^3\)\(^8\), 115-116
During deposition, an ethanol/water cooling system was used to control the substrate temperature at 0°C to 40°C. The as-deposited metals were sculpted into helices by unidirectional rotation of the substrates clockwise/counterclockwise to generate right/left-handed NPs. A helix is morphologically characterized by helical pitch ($P$), number of pitches ($n$), wire diameter ($d$), height ($H = nP + d$), and coil diameter ($D$). GLAD enables one to facilely control $P$ and $n$. $P$ (in units of nm) is engineered by

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

where $R_r$ is the rate of substrate rotation in unit of degrees per second, and $R_d$ is the deposition rate of metals on the substrate at a given $\alpha$. At $\alpha$ of 86°, $R_d$ was calibrated as 0.045 nm/s for Ag, 0.08 nm/s for Al, and 0.078 nm/s for Cu. $n$ is equal to the number of circles that a substrate is rotated. For example, when $R_r$ was increased from 0.07 to 5.0°/s, Ag was sculptured to form AgNHs with a $P$ of 231.4 nm to AgNPs with $P$ of 3.2 nm.

At a deposition angle of 0° and $T_{sub}$ of approximately 0°C, a substrate that was not rotated was deposited with 10- to 30-nm-thick metal, leading to the generation of PhNPs without hidden chirality for control experiments.

### 2.1.2 GLAD of the host@guest NPs

In the following Chapter 4, the host of chiral NPs was made from Cu and iron oxide. Analogous to the deposition of chiral PhNPs, that of the chiral host was performed at $\alpha$ of 86°, $T_{sub}$ of approximately −40°C, and a deposition rate of 0.3 nm/s as monitored by the QCM, using an electron-beam accelerating voltage of 8.0 kV and emission current of 30 to 40 mA for Cu pellets (99.9999%, Torsh Technology Limited) and 35 to 45 mA for Fe$_2$O$_3$ powder (99.99%, Torsh Technology Limited).
Without substrate rotation, the guest Al was deposited at $\alpha$ of 0°, $T_{sub}$ of approximately −40°C, and $R_d$ of 0.1 nm/s. It used an electron-beam accelerating voltage of 8.0 kV and emission currents of 25 mA for Al, 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 to 30 nm, monitored by the QCM. To generate the achiral host (CuNPs and Fe$_3$O$_y$NPs)@Al, the host material (Cu and Fe$_2$O$_3$) and Al were then deposited at $\alpha$ of 0° and $T_{sub}$ of approximately 0°C without substrate rotation. The nominal thicknesses of Cu, iron oxide, and Al were controlled as 25, 40, and 30 nm, respectively. 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.

### 2.1.2 Photocyclodimerization of AC on PhNPs

Photocyclodimerization of AC on PhNPs is processed in Chapter 4. PhNPs (including AgNPs and CuNPs with diverse $P$) were rinsed with 5% HF solution and deionized water. After drying, the as-treated samples were immersed in an ethanol solution containing 0.5 mmol/L AC (TCI Chemicals) for 1 h and dried in ambient conditions. Photocyclodimerization of AC on the PhNPs was performed in a nitrogen-filled environment at 0°C and irradiated with an LED lamp with a wavelength of 365 nm for 12 h. The photolyzed samples were transferred to 1% NaOH solution (0.3 ml) for 1 h of ultrasonication, and the ultrasonicated solution was then applied to the high-performance liquid chromatography (HPLC) analysis.

### 2.1.3 HPLC

HPLC analysis was carried out at 35°C on the tandem columns (Inertsil ODS-2 and Chiralcel OJ-R diluted) by 0.1% TFA in H$_2$O and acetonitrile (62:38 by volume) at a flow rate of 0.5 ml/min. The $ee$ value was evaluated by measuring the area of the two peaks assigned to the chiral product 3 in the HPLC chromatogram.
2.2 mp-SiNWs

2.2.1 1-MACE

SiNWs were fabricated by MACE of Si wafers polished on one side (Semiconductor Wafer, Inc.), including n−/n+/n−2-Si(100) and n+/n+2-Si(111). The wafers in an area of 1.5 × 1.5 cm² were cleaned via ultrasonication in acetone and ethanol, degreased in piranha solution (98% H₂SO₄/30% H₂O₂ = 3:1, v/v) at room temperature, and dipped in 5% HF to remove native oxides. The treated wafers were then etched by MACE to create a random array of SiNWs without solar illumination or solution stirring. The conditions of MACE are summarized in each chapter. After MACE, the etched wafers were immediately dipped into 68% HNO₃ to dissolve the MACE-generated Ag dendrites covering the wafers. After each acid treatment, the wafers were thoroughly rinsed with deionized water (18.2 MΩ, Milli-Q reference water purification system fed with campus distilled water) and sufficiently dried with N₂.

2.2.2 Bi-MACE

Analogous to 1-MACE, heavily doped Si(100) wafers (i.e., n−2–Si (100) with one side polished, doped with As, and electrical resistivity of 1 to 5 m Ω·cm (Semiconductor Wafer, Inc.) were etched by MACE. This is the first MACE. The as-generated mp-SiNWs were then taped off and transferred to a transparent tape (3M, Scotch). The taped wafer was treated by the second MACE under the same conditions as the first MACE.

2.2.3 Etching in 40% aqueous NH₄F

To fully investigate the etching effects of 40% aqueous NH₄F on SiNWs, the etching process is followed in this way. A wafer (1.5 × 1.5 cm²) with as-generated
NW arrays was cut into small pieces and then immediately etched in 150 mL of NH₄F (40 wt % in H₂O, pH ≈ 8, Aldrich). The etching duration varied from 0 to 10 min. When the etching was complete, the samples were immediately rinsed with deionized water and dried with N₂.

2.2.4 Thermal monosilylation

At a modest temperature, 1,4-diethynylbenzene (DEBZ) is monosilylatedly grafted on H-terminated mp-SiNWs. In a three-necked flask fitted with an argon inlet, a thermometer, and a reflux condenser, thermal hydrosilylation was carried out in mesitylene (99%, extra pure, Acros Organics) with 0.2 mol/L DEBZ. The as-generated SiNWs were dipped in 5% HF for 15 min to create H-terminated surfaces. After sufficient rinsing with deionized water and drying with N₂, the H-terminated samples were immediately transferred into the hydrosilylation solution, which had been deoxygenated with Ar for 1 h. The pre-deoxygenated solution with the H-terminated samples was continuously deoxygenated for another 1 h. During hydrosilylation, the three-necked flask was fully filled with Ar without directly bubbling the solution to inhibit the grafting from disturbing. The flask was immersed in an oil bath to stably control the reaction temperature at 110°C, and hydrosilylation was performed up to 20 h. After modest hydrosilylation, the samples were rinsed with dichloromethane (anhydrous, ≥99.8%) and ethanol and dried with N₂.

2.3 Characterization

2.3.1 Measurement of spectra

BioLogic CD (MOS 500) and DSM 1000 CD (Olis Inc.) were used to monitor the CD spectra of AgNPs and AgNSs, respectively, deposited on sapphire under circularly polarized incident light along the substrate normal. The sample was
rotated clockwise at 0.2 rpm to monitor the CD in the wavelength range of 200 to 800 nm to eliminate linear birefringence. Eight CD spectra were then recorded and algebraically averaged to obtain a CD spectrum of the sample. The UV–visible extinction spectra of all samples were measured using BioLogic CD (MOS 500).

A spectroscopic ellipsometer (SOPRA, model GES5E) was used to measure s- and p-polarized specular reflection from the samples, and an aluminum layer deposited on an Si wafer was used as the reference background.

A homemade PL system was set up to measure the PL of the samples in ambient conditions under the excitation of an He-Cd laser (325 nm, 15 mW, IK3151R-E, Kimmon Koha Co.).

ATR-FTIR (PerkinElmer Spectrum Two, with a horizontal ATR accessory from PIKE Technologies, germanium crystal, DTGS IR detector, at an incident angle of 45°).

### 2.3.2 Structure characterization

The as-deposited samples were mechanically split, leaving freshly exposed surfaces for the characterization with scanning electron microscopy (Oxford, LEO 1530). The NPs were scratched off the substrates and well dispersed in ethanol via ultrasonication for 5 min. Several drops of the mixture were applied to a lacey carbon film on a grid structure (Electron Microscopy Sciences). The grid was dried in ambient conditions and inspected with transmission electron microscopy with low resolution (Tecnai G2 20 STWIN) and high resolution (Tecnai F20 microscope, FEI, 200 kV; a CM-120 microscope [Philips, 120 kV] coupled with an EDX spectrometer [Oxford Instruments]).

Without post-deposition treatment, the samples were characterized by X-ray diffraction (XRD, Bruker, nonmonochromated Cu Kα x-ray with wavelength of
0.15418 nm, Advance D8 multipurpose x-ray diffractometer) and X-ray photoelectron spectroscopy (XPS, Sengyang SKL-12, non-monochromatic Mg Kα radiation of 1253.6 eV, a current of 15 mA, voltage of 10 kV, and takeoff angle [between the sample and detector] of 90° in a vacuum of approximately $2 \times 10^{-9}$ mbar).
Chapter 3 Plasmonic helical Nanoparticles with Chiroptical Activity Originating from Hidden Helicity

GLAD provides one-step, wafer-scale production of helical metamaterials on various kinds of substrates (e.g., opaque, transparent, conducting, insulating, and flexible substrates), paving the way for functional devices.

A helix is geometrically described by helical pitch \( P \), coil diameter \( D \), wire diameter \( d \), number of helical pitch \( n \), and height \( H = nP \). Helical structures play an essential role in chiroptical activity, which is primarily characterized by circular dichroism (CD) evaluating the difference in optical absorption/extinction of left- and right-handed circularly polarized light. Only \( P \) and \( n \) of a helix can be readily, flexibly engineered by GLAD, and inevitably \( D \) and \( d \) tend to rise with increasing \( P \). As a result, attention has been paid to the study of \( P \)-dependent chiroptical activity. Numerical simulation has predicted the blue shift of CD with shrinking \( P \), consistent with experimental results showing that plasmonic microspirals (with \( P > 1 \) \( \mu \)m) have chiroptical activity in the wavelength of 3–6.5 \( \mu \)m, while nanohelices (NHs; with \( P < 100 \) nm) have chiroptical response in the UV-visible-near infrared region. It is of fundamental interest to study chiroptical activity approaching the physical limit where \( P \) is minimized to sub-10 nm comparable to molecular sizes, about which little is known. However, the minimization of \( P \) is physically constrained by the geometrical prerequisite of \( P > d \) to form a helix. \( d \) of a helix inevitably rises with increasing substrate temperature \( (T_{sub}) \) because of the thermal activation of surface diffusion of adatoms. Fischer et al. used liquid N\(_2\) to control \( T_{sub} \) as low as \(-170^\circ\)C and generated plasmonic NHs with \( P \) of 20 nm, the smallest reported so far. The sub-10-nm minimization of \( P \) technically requires further substrate cooling; however, it
would be difficult to operate GLAD reliably with the integration of such an extremely-low-$T_{sub}$ cooling system.

Herein, neglecting the geometrical limit of helices, we operate the GLAD processes that produce plasmonic NHs to generate silver NPs (AgNPs) with $P < d$, at $T_{sub}$ of roughly 0 °C under which $d$ is not smaller than 60 nm. AgNPs appear not to have helical structures, but are chiroptically active in the UV-visible region. The nominal $P$ can be minimized to as small as 3.5 nm, where AgNPs have reliably detectable chiroptical response. Characterized by CD and extinction spectroscopies, the chiroptical activity of AgNPs is systematically studied as a function of $P$ in a range of 3.5–70 nm.

The engineering of structural parameters of RH/LH-AgNPs-$P$ is summarized in Table 3.1. When $R_r$ was reduced to 0.07 °/s, Ag was sculptured to form AgNSs with $P$ of 231.4 nm.

### 3.1 Results and discussion

A close-packed array of AgNPs was deposited by GLAD, having $H$ of ~100 nm and nominal $P$ engineerable in a range of 3–70 nm (Figure 3.1). The hidden chirality was controlled by substrate rotation: counterclockwise rotation produces left-handed AgNPs (Figure 3.1a, c, e, i, k, m), and clockwise rotation generates right-handed AgNPs (Figure 3.1b, d, f, h, j, l, n). For easy differentiation, left-handed AgNPs with a nominal $P$ are denoted LH-AgNPs-$P$, whose mirror images are denoted RH-AgNPs-$P$. $P$ was evaluated by measuring $H$ and $n$, given by $P = H/n$ (Table 3.1). For instance, LH-AgNPs-9.8 represents left-handed AgNPs with a nominal $P$ of 9.8 nm (Figure 3.2).
Figure 3.1 Cross-sectional SEM images of AgNPs: nominal \( P \) of (a) 3.8, (b) 3.5, (c) 7.1, (d) 7.0, (e) 9.8, (f) 10, (g, h) 17, (i) 32, (j) 31, (k) 49, (l) 47, (m) 66, and (n) 63 nm; hidden chirality of left-handedness (LH: a, c, e, g, i, k, m) and right-handedness (RH: b, d, f, h, j, l, n). (a–n) have a scale bar of 100 nm, as shown in (a). Insets on the top: schematic diagrams of LH- and RH-AgNPs.
Figure 3.2 UV-visible spectral characterization of LH- (red lines) and RH-AgNPs (blue lines) with nominal $P$ of $\sim 10$ nm: (a) extinction; (b) CD; (c) anisotropy $g$ factor. Insets: $\lambda_{\text{max}}$ is the LSPR wavelength, and cyan arrows mark the shoulder plasmonic peaks.

Table 3.1 Engineering of helical pitch $P$. $P_d$ represents the designed $P$. $R_d$ (the deposition rate of Ag) was controlled at 0.045 nm/s, calibrated at the deposition angle of 86° with respect to the direction normal to the substrate. For each sample, multiple (not less than 10) measurements were performed to evaluate $H$ with algebraic average value and standard deviation.

<table>
<thead>
<tr>
<th>$R_c$ (°/s)</th>
<th>$P_d$ = 360 $R_d/R_c$ (nm)</th>
<th>$H$ (nm)</th>
<th>$n$</th>
<th>$P = H/n$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LH</td>
<td>RH</td>
<td>LH</td>
<td>RH</td>
</tr>
<tr>
<td>0.07</td>
<td>231.4</td>
<td>238 ± 11</td>
<td>215 ± 4</td>
<td>1</td>
</tr>
<tr>
<td>0.23</td>
<td>70.4</td>
<td>95 ± 4</td>
<td>90 ± 6</td>
<td>1.4</td>
</tr>
<tr>
<td>0.3</td>
<td>54.0</td>
<td>91 ± 4</td>
<td>87 ± 5</td>
<td>1.9</td>
</tr>
<tr>
<td>0.5</td>
<td>32.4</td>
<td>92 ± 4</td>
<td>95 ± 4</td>
<td>2.9</td>
</tr>
<tr>
<td>1.0</td>
<td>16.2</td>
<td>97 ± 8</td>
<td>94 ± 5</td>
<td>5.6</td>
</tr>
<tr>
<td>1.5</td>
<td>10.8</td>
<td>90 ± 7</td>
<td>94 ± 4</td>
<td>9.2</td>
</tr>
<tr>
<td>2.3</td>
<td>7.0</td>
<td>99 ± 5</td>
<td>98 ± 5</td>
<td>14.0</td>
</tr>
<tr>
<td>5.0</td>
<td>3.2</td>
<td>113 ± 7</td>
<td>104 ± 6</td>
<td>30.0</td>
</tr>
</tbody>
</table>

The LH/RH-AgNPs-10 arrays have a broad UV-visible extinction reaching its maximum amplitude at the wavelength of $\sim 370$ nm (Figure 3.2a), ascribed to localized surface plasmon resonance (LSPR). The single-peak extinction feature is
ascribed to the fact that the aspect ratio of H/D, evaluated as 1.3 for LH-AgNPs-9.8 and 1.4 for RH-AgNPs-10 (Figure 3.3), is close to 1. Correspondingly, the arrays have chiroptical response at wavelengths of 330–700 nm, characterized by CD (Figure 3.2b). The CD spectra are composed of the plasmonic peak at 370 nm, a peak at ~340 nm, and bisignated peaks in the visible region. The 340-nm CD peak is assigned to the shoulder plasmonic mode, as there is a shoulder extinction peak at 340 nm. Our numerical simulation revealed that the visible chiroptical activity stems from the optical interaction (including reflection, scattering and/or trapping) of the AgNP array.119 The shoulder plasmonic and visible modes are chiroptically weaker than the plasmonic mode. The anisotropy g factor can be calculated by

\[ g = \frac{CD}{16500A} \]  

where CD is the ellipticity (units: millidegree, or mdeg) and A is the extinction. The arrays have the plasmonic g factor of ~4×10^{-3} (Figure 3.2c). The CD spectrum flips around the zero-CD axis as the hidden chirality is switched, illustrating that the hidden helicity leads to intrinsic chiroptical activity of AgNPs with \( P < d \). The chiroptical origin can be further demonstrated by the fact that without substrate rotation, the deposited AgNPs lack hidden chirality and chiroptical response (Figure 3.5).
Figure 3.3 Plot of aspect ratio ($H/D$) versus nominal $P$ of LH- (red circles) and RH-AgNPs (blue squares).

Figure 3.4 UV-visible spectral characterization of LH- (red lines) and RH-AgNPs (blue lines) with nominal $P$ as inset: (a) extinction; (b) CD.

In general, chiral AgNP arrays with a nominal $P$ in the range of 3–70 nm have chiroptical response in the UV-visible region (Figure 3.4). The hidden chiroptical activity will be briefly discussed. First, LSPR barely shifts with nominal $P$ (Figure 3.4a and 3.6a); neither do the (shoulder) plasmonic CD (Figure 3.4b and 3.6b) and $g$ factor (Figure 3.6c) modes. As well known, the LSPR substantially correlates to NP structures. Varying with nominal $P$, AgNPs tend to have a relatively small distribution of the aspect ratio of $H/D$ that is evaluated as $1.4 \pm 0.2$ (Figure 3.3), accounting for the small LSPR spectral shift with increasing nominal $P$. Second, the plasmonic CD (and $g$ factor) mode tends to have a common logarithmic increase with nominal $P$ (Figure 3.6 and 3.6d). The chiroptical amplification slope can be evaluated by
\[ k_{l|g(CD)} = \frac{d|g_{CD}|}{dP} \quad (3.2a) \]
\[ k_{l|g(g)} = \frac{d|g_{g}|}{dP} \quad (3.2b) \]

where \( CD_{\text{max}} \) and \( g_{\text{max}} \) represent the amplitude of CD and \( g \) factor at the wavelength of \( \lambda_{CD,\text{max}} \) and \( \lambda_{g,\text{max}} \), respectively.

**Figure 3.5** Ag thin film with nominal thickness of 10 nm, deposited at an incident angle of 0° with respect to the direction normal to the substrate. The substrate was not rotated during the deposition. (a) Cross-sectional SEM image; (b) CD (black line) and extinction (red line) spectra.
Figure 3.6 Plots of (a) $\lambda_{\text{Ext,max}}$, (b) $\lambda_{\text{CD,max}}$, (c) $\lambda_{g,max}$, (d) $|g_{\text{max}}|$ of the plasmonic mode versus nominal $P$ of LH- (red circles) and RH-AgNPs (blue squares). (d) The plots are linearly fitted to evaluate the slopes $k_{lg(g)}$ as inset. (b) $\lambda_{\text{CD,max}}$ of the shoulder plasmonic mode is highlighted with cyan background.

Figure 3.7 (a) Plots of $|CD_{\text{max}}|$ versus nominal $P$ of AgNPs, in terms of the hidden chirality (LH: red circles; RH: blue squares) and CD modes (the plasmonic mode: solid symbols, highlighted with green background; the shoulder plasmonic mode: hollow symbols, highlighted with cyan background). The plots are linearly fitted to evaluate the slopes $k_{lg(CD)}$ summarized in (b).

The slope of the plasmonic mode varies in a small range of 0.021–0.026 nm$^{-1}$ with the hidden AgNP chirality, and is nearly equal to that of the shoulder plasmonic mode (Figure 3.7b). The extinction cross section of AgNPs rises with increasing nominal $P$, accounting for the amplification of chiroptical activity. Third, the visible mode also increases the CD amplitude with increasing nominal $P$ (Figure 3.7b). The visible chiroptical mode originates from the optical interaction of the AgNP arrays, so as to vary sensitively with the spacing and NP structure of the AgNP array. On a flat surface, GLAD typically generates a random array with little reproducible control of the spacing. GLAD was operated at $T_{sub}$ of 0 °C, at which Ag adatom diffusion on the deposited AgNPs could not be effectively prohibited; hence, AgNPs appear to have irregular structures. As a result, the array has the broad extinction feature in the visible regime, and the visible chiroptical mode
sometimes has irregular CD signals, making it difficult to quantitatively investigate the chiroptical dependence on nominal $P$.

### 3.2 Conclusion

We neglect the helix geometrical limit of $P > d$ and operate GLAD under fast substrate rotation to generate AgNPs having hidden helicity with nominal $P < d$. Stemming from the hidden helicity, the AgNPs 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 deposition is operated at regular $T_{\text{sub}}$ to avoid the integration of GLAD with an extremely low-$T_{\text{sub}}$ 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 plasmonics 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). 42
Chapter 4 Ultraviolet-Visible Chiroptical Activity of Aluminum Nanostructures

Biomolecules typically absorb UV light with a wavelength ($\lambda$) shorter than 250 nm; but they usually have such a sub-wavelength size that can barely perceive the circular polarization of CPL, leading to low chiroptical activity.\(^{11}\) To effectively enhance the chiroptical activity of biomolecules, it has been proposed to amplify an optical chirality (denoting chirality density) of CPL in the UV range,\(^{12-13}\) so as to enhance CPL absorption of biomolecules. Numerical simulation reveals that chiral metamaterials can resonantly enhance the optical chirality of CPL in the vicinity of their surfaces at a $\lambda$ corresponding to localized surface plasmon resonance (LSPR).\(^{14}\) Therefore, it causes a fundamental demand on producing chiral metamaterials with LSPR and chiroptical activity (i.e., resonant CD) in the UV region.\(^{15}\)

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. Aluminum (Al) is a practically promising material to generate UV-active plasmons,\(^{50}\) due to its natural abundance on earth, low cost, and facile processing.\(^{51}\) LSPR of Al nanoparticles (AlNPs) can be tailored in the UV-visible region, as a function of NP size and the percentage of Al$_2$O$_3$ in the AlNPs.\(^{52-53}\) Chiral AlNPs, fabricated by an asymmetric deposition of Al on the chiral shaped etch pits, exhibit a set of bisignate CD peaks at $\lambda$ of 250 – 700 nm, and the near-field electromagnetic simulation shows a five-fold enhancement in the optical chirality for the UV and visible resonance.\(^{54}\) 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. 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, which is lack for Al. Furthermore, we found that during the electron-beam evaporation of GLAD, the melted Al is apt to flowing out of a crucible to cause a short circuit and terminate the GLAD. As a result, GLAD of Al could only be operated in a short period of time, e.g., ~30 min, within which the deposition of Al nanohelices usually could not be finished.

Herein, we devise two GLAD-related approaches to quickly deposit chiral Al nanostructures that exhibit strong chiroptical activity in the UV-visible region. One is to deposit AlNPs with hidden helicity where \( P \) is smaller than wire diameter \( (d) \), using the fast-substrate-rotation method we reported previously; another is to deposit an achiral thin layer of Al on chiral copper NPs (i.e., CuNPs) for generating UV-visible chiroptical response via chirality transfer from the chiral host to the achiral guest. In the two methods, it takes no more than 30 min to deposit Al. The helicity of RH/LH-host NPs is summarized in Table 4.1.

The chiral Al nanostructures are systematically characterized in terms of morphology, surface oxidation, crystallinity, and UV-visible CD. The mechanism of chirality transfer 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.
4.1 Results and Discussion

4.1.1 Chiral aluminum nanostructures with UV-visible chiroptical activity

GLAD with fast substrate rotation enables one to generate helical structures with $P < d$ \cite{42}, resulting in the deposition of chiral AlNPs with hidden handedness (i.e., the helical arrangement of core/surface atoms in the AlNPs that cannot be observed using SEM or TEM, Figure 4.1 and Figure 4.3). Anticlockwise rotation is operated to sculpture the AlNPs as left-handed (LH-AlNPs, Figure 4.1a), and clockwise rotation results in the right-handed AlNPs (RH-AlNPs, Figure 4.1b).

![Chiral AlNPs with hidden (a) left handedness (LH) and (b) right handedness (RH), a nominal pitch ($P$) of ~30 nm, and height ($H$) of ~120 nm. (a, b) Top-down SEM images. TEM images of a LH-AlNP: (c) low resolution, (d) high resolution to show native oxidation and the (200) plane. (e) XPS spectrum of Al2p of the natively oxidized LH-AlNPs (i.e., LH-AlNPs:Al2O3). (f) XRD spectra of LH- and RH-AlNPs:Al2O3, and the peaks marked by asteroid are ascribed to the sapphire substrate on which the AlNPs were deposited. UV-visible spectra](image)

Figure 4.1 Chiral AlNPs with hidden (a) left handedness (LH) and (b) right handedness (RH), a nominal pitch ($P$) of ~30 nm, and height ($H$) of ~120 nm. (a, b) Top-down SEM images. TEM images of a LH-AlNP: (c) low resolution, (d) high resolution to show native oxidation and the (200) plane. (e) XPS spectrum of Al2p of the natively oxidized LH-AlNPs (i.e., LH-AlNPs:Al2O3). (f) XRD spectra of LH- and RH-AlNPs:Al2O3, and the peaks marked by asteroid are ascribed to the sapphire substrate on which the AlNPs were deposited. UV-visible spectra
of the AlNPs:Al₂O₃ arrays: (g) extinction (i.e., Ext), (h) CD (inset: CD spectra in a \( \lambda \) range of 500 – 700 nm), and (i) anisotropic \( g \)-factor. (f-i): LH-AlNPs:Al₂O₃ (red lines), RH-AlNPs:Al₂O₃ (blue lines).

The chiral AlNPs have a nominal \( P \) of \( \sim 30 \) nm, height \( (H) \) of \( \sim 120 \) nm, and number of pitch \( (n) \) of 4, but appear not to have a helical structure (Figure 4.1c, d). Under ambient conditions the chiral AlNPs are spontaneously oxidized and covered with an Al₂O₃ layer (characterized by XPS, Figure 4.1e) with a thickness of 2–3 nm (Figure 4.1d), coincident with the previous results. The AlNPs have crystalline structures (Figure 4.1d, f). The array of chiral AlNPs has an extinction increasing from the visible to UV range (Figure 4.1g), The extinction spectrum doesn’t exhibit a clear maximum, probably due to the wide distribution of particle diameter (\( DNP, \) inset in Figure 4.1g, and Table 4.2).

Table 4.1 Summary of the helicity of chiral NPs. \( P_d \) is the designed \( P \), according to eq. 2.1. \( R_d \) (the deposition rate) was controlled and calibrated at \( \alpha \) of 86° to be 0.08 nm/s for Al, Cu and Fe₂O₃, and 0.04 nm/s for Ag. For each sample, multiple (not less than 10) measurements were operated to statistically evaluate \( H \) having an algebraic average value and standard deviation. The ratio of standard deviation to algebraic average value is calculated, as shown in percentage following the standard deviation.

<table>
<thead>
<tr>
<th>Chiral NPs</th>
<th>( R_d ) (( \ell^2/s ))</th>
<th>( P_d = 360 \frac{R_d}{R_f} ) (nm)</th>
<th>( H ) (nm)</th>
<th>( n )</th>
<th>( P = \frac{H}{n} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LH</td>
<td>RH</td>
<td>LH</td>
<td>RH</td>
<td>LH</td>
</tr>
<tr>
<td>Al</td>
<td>1.0</td>
<td>30.0</td>
<td>126 ± 8 (6.3%)</td>
<td>112 ± 7 (6.2%)</td>
<td>4.0</td>
</tr>
<tr>
<td>Ag</td>
<td>3.0</td>
<td>5.4</td>
<td>40 ± 5 (12.5%)</td>
<td>43 ± 4 (9.3%)</td>
<td>9.1</td>
</tr>
<tr>
<td>Cu</td>
<td>7.9</td>
<td>3.6</td>
<td>40 ± 2 (5.0%)</td>
<td>40 ± 1 (2.5%)</td>
<td>13.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.0</td>
<td>5.0</td>
<td>41 ± 3 (7.3%)</td>
<td>40 ± 2 (5.0%)</td>
<td>8.0</td>
</tr>
</tbody>
</table>

\( DNP \) of the chiral AlNPs were statistically analyzed to have an algebraic average value and standard deviation, and the size distribution can be evaluated by calculating the ratio of standard deviation to average value. Small size distribution
is generally regarded to have the ratio less than 10%. The ratio of the LH-AlNPs is 28.3% and that of RH-AlNPs is 19.0%, illustrating that the chiral AlNPs have a relatively wide distribution of $D_{NP}$.

**Table 4.2** Summary of particle diameter ($D$) of the chiral AlNPs and diverse host@guest nanostructures. For each sample, multiple (not less than 10) measurements were operated to statistically evaluate $D$ having an algebraic average value and standard deviation. The ratio of standard deviation to algebraic average value is calculated, as shown in percentage following the standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>Handedness</th>
<th>AlNPs</th>
<th>Cu@Al</th>
<th>Fe$_x$O$_y$@Al</th>
<th>Ag@Au</th>
<th>Ag@Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ (nm)</td>
<td>LH</td>
<td>54 ± 14</td>
<td>57 ± 12</td>
<td>55 ± 12</td>
<td>49 ± 6</td>
<td>50 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(26.0%)</td>
<td>(21.1%)</td>
<td>(21.8%)</td>
<td>(12.2%)</td>
<td>(6.0%)</td>
</tr>
<tr>
<td></td>
<td>RH</td>
<td>56 ± 15</td>
<td>51 ± 4</td>
<td>54 ± 9</td>
<td>58 ± 5</td>
<td>48 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(26.7%)</td>
<td>(7.8%)</td>
<td>(16.7%)</td>
<td>(8.6%)</td>
<td>(10.4%)</td>
</tr>
</tbody>
</table>

In the UV-visible region, the chiral AlNPs exhibit a broadband chiroptical activity characterized by CD (Figure 4.1h). The CD spectrum of the chiral AlNPs flips around the zero-CD axis while the hidden handedness is switched, illuminating that the AlNPs are chiroptically active intrinsically attributed to the hidden helicity. It was reported that $P$ plays an essential role in determining the chiroptical activity of the plasmonic chiral NPs. The chiral AlNPs exhibit a narrow distribution of $P$ (less than 6.5%, Table 4.1), so as to have the well-defined chiroptical activity. An anisotropy $g$ factor is calculated to normalize the chiroptical activity in terms of surface density and NP height of the NP arrays, given by

$$g = \frac{CD}{16500Ext}$$  \hspace{1cm} (1)

where CD is the ellipticity (units: millidegree, or mdeg), and Ext is the extinction. The chiral AlNPs exhibit very strong chiroptical activity with an anisotropy $g$ factor of 0.01 – 0.02 in the $\lambda$ range of 250–500 nm (Figure 4.1i), which is comparable to that of the chiral colloidal AlNPs.\textsuperscript{54} The chiral AlNPs have a very stable chiroptical
activity (Figure 4.3c), because the native Al₂O₃ can effectively prohibit further spontaneous oxidation and chiroptical degradation. Note that the AlNP arrays with opposite handedness have some asymmetrical chiroptical activity, e.g., at a λ of ~400 nm (Figure 4.1i). The asymmetry may be ascribed to non-uniform distribution of the helical structures in the random AlNP array.

Figure 4.2 Chirality transfer from the host of chiral CuNPs (with a P of 3 nm and H of 40 nm) to the guest of Al (with a nominal thickness of 30 nm). Top-down SEM images (with a scale bar of 100 nm): (a, c) LH-CuNPs, (b, d) RH-CuNPs without (a, b) and with (c, d) the deposition of Al. TEM images of a LH-CuNP@Al: (e) low resolution, (f) high-resolution (inset: EDX spectrum). UV-visible spectra of the NP arrays: (g) extinction, (h) CD and (i) anisotropic g-factor; the host of chiral CuNPs covered by native oxides (CuNPs:CuO where CuO denotes the copper oxides with unknown stoichiometry, dotted lines), CuNPs@Al (host@guest, solid lines), LH (red lines), and RH (blue lines). Green and cyan backgrounds highlight the spectra of the host and guest, respectively. Inset in (g): visible extinction spectra of the host in a λ range of
500 – 700 nm. (h) The ellipticity of the chiral host (dotted lines) is amplified by 5 times for clarity.

Chiroptical activity can be imposed on achiral Al nanostructures (denoted the guest) that are deposited on chiral plasmonic NPs (denoted the host), that is, the chiral host@achiral guest nanostructures (e.g., the chiral CuNPs@Al, Figure 4.2). LH- (Figure 4.2a) and RH-CuNPs (Figure 4.2b) were deposited using the fast-substrate-rotation GLAD technique, the same as that for generating the chiral AlNPs. The chiral CuNPs, with a nominal P of ~3 nm, H of 40 nm and n of ~13.5, have crystal structures (Figure 4.2f). The chiral CuNPs are natively oxidized under ambient conditions, i.e., CuNPs:CuO in which CuO represents copper oxides with unknown stoichiometry. The chiral CuNPs:CuO exhibit LSPR at a $\lambda$ of ~600 nm (inset in Figure 4.2g), and have weak resonant CD at $\lambda > ~550$ nm (dotted lines, Figure 4.2h, i). The weak chiroptical response can be ascribed to the small nominal $P$ of ~3 nm. They have negligible chiroptical response in the $\lambda$ range of 200 – 500 nm (Figure 4.2i).

![Image](image_url)

**Figure 4.3** Ambient aging of the chiroptical activity of LH-AlNPs:Al$_2$O$_3$ (with a $P$ of 14 nm and $H$ of 56 nm) characterized by UV-visible extinction (dashed lines) and CD (solid lines) spectra, as a function of aging duration: 0 (black lines), 15 (red lines), 43 (green lines) and 52 (blue lines) days.

As we know, the chiroptical activity of the chiral NPs intrinsically stems from the helicity induced by the substrate rotation during GLAD. Without substrate rotation, a layer of Al, deposited on a smooth surface at a deposition angle ($\alpha$) of 0° with respect to the direction of the substrate normal, is chiroptically inactive in the UV-
visible region (blue lines, Figure 4.5). Although the Al thin film exhibits a CD peak with a maximum ellipticity of ~2 mdeg at a $\lambda$ of ~500 nm (Figure 4.5b), the maximum ellipticity is close to the CD detection limit and has an anisotropic $g$ factor less than $1 \times 10^{-4}$. It is illustrated that the Al thin films deposited under no substrate rotation don't have chiroptical response. When the achiral Al thin film was deposited onto the chiral CuNPs that weren’t natively oxidized in the vacuumed GLAD chamber, the CuNPs appear to be enlarged in size (Figure 4.2c, d) due to the capping of Al nanostructures (i.e., chiral CuNPs@Al, Figure 4.2e). The coating of Al was verified by EDX (inset of Figure 4.2f), XRD (Figure 4.4a) and XPS (Figure 4.4b). Analogous to the chiral AlNPs, the Al nanocappings have crystalline structures (Figure 4.5a) and are spontaneously oxidized (Figure 4.2f and 4.5b). The capping of Al tends to screen the XRD signals of the underneath host of CuNPs (Figure 4.5a), and cause a new chiroptical response in the $\lambda$ range of 250 – 500 nm (solid lines, Figure 4.2h, i). Given the negligible chiroptical activity of the chiral host in this range, the new UV-visible chiroptical activity could be ascribed to the Al nanocappings. Chirality transfer from the chiral host to the achiral guest probably accounts for the induced CD of the achiral Al nanocappings, because the chiroptical induction wasn't observed when the achiral Al thin film was deposited onto the host of achiral CuNPs (red lines, Figure 4.3). Simultaneously, the chiroptical activity of the host in the $\lambda$ range of 500–600 nm is enhanced by the Al nanocappings (solid lines versus dotted lines, Figure 4.2i). The host-induced chiroptical activity of the Al nanocappings is roughly in one order of magnitude lower than the intrinsic chiroptical activity of the chiral AlNPs (solid lines, Figure 4.2i versus 4.1i). It may be ascribed to partial coating of Al on the chiral host (Figure 4.2e), leading to partial chirality transfer from the chiral host to the achiral guest.
**Figure 4.4** Characterization of the chiral CuNPs@Al. (a) XRD spectra: LH (red line), RH (blue line). The peaks marked by asteroid are ascribed to the sapphire substrate, and the other peaks are assigned to the guest of Al. (b) XPS spectrum of Al2p of LH-CuNPs@Al.

**Figure 4.5** UV-visible spectra of (a) extinction, (b) CD and (c) anisotropic $g$-factor: achiral CuNPs@Al (a nominal thickness of 25 nm for the host and 15 nm for the guest, red lines), and an achiral Al thin film with a nominal thickness of 30 nm (blue lines).
4.1.2 Mechanism of chirality transfer

The host@guest chirality transfer may be ascribed to plasmonic coupling and helicity duplication, similar to the case that achiral plasmonic NPs are chiroptically induced by chiral ligands. It has been proposed that the plasmonic coupling occurs via near-field dipolar/multipolar coupling, far-field electrodynamic coupling, and electronic orbital hybridization; the helicity duplication of achiral plasmonic NPs from chiral ligands leads to the formation of chiral metal cores, transfer of chiral footprints to nanocluster surfaces, and creation of Au-S based staple motifs that are arranged in a chiral fashion on nanocluster surfaces.

To solely study the mechanism of helicity duplication, the chiral host was made from non-plasmonic materials (e.g., iron oxides) to eliminate the contribution of plasmonic coupling. Analogously, the fast-substrate-rotation GLAD was used to produce the chiral iron oxide NPs having a $P$ of 5 nm, $H$ of 40 nm, and $n$ of 8 (Figure 4.6a, b).
Figure 4.6  Chirality transfer from the host of chiral iron oxide (Fe\textsubscript{x}O\textsubscript{y}) NPs (with a P of 5 nm and H of 40 nm) to the guest of Al (with a nominal thickness of 30 nm). Top-down SEM images: (a, c) LH-Fe\textsubscript{x}O\textsubscript{y}NPs, (b, d) RH-Fe\textsubscript{x}O\textsubscript{y}NPs without (a, b) and with (c, d) the deposition of Al. UV-visible spectra of the NP arrays: (e) CD and (f) anisotropic $g$-factor; LH (red lines), RH (blue lines), the host (dotted lines), the host@guest (solid lines), and achiral Fe\textsubscript{x}O\textsubscript{y}NPs@Al (black lines).

The composition of the host was characterized by XPS (Figure 4.7). The XPS peaks of Fe2p were fitted to be composed of a weak peak at bond energy of 718 eV that is assigned to Fe\textsubscript{2}O\textsubscript{3}, one at 712 eV assigned to Fe\textsuperscript{3+} and the other at 710 eV assigned to Fe\textsuperscript{2+} (Figure 4.7a); and that of O1s was fitted to be composed of one at 529.9 assigned to a typical state of O\textsuperscript{2-} species corresponding to Fe\textsubscript{3}O\textsubscript{4} (Figure 4.7b).\textsuperscript{140} It is revealed that the as-deposited NPs are composed of Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} with unknown weight percentage (denoted Fe\textsubscript{x}O\textsubscript{y} where 2 < x < 3 and 3 < y < 4).

However, the chiral Fe\textsubscript{x}O\textsubscript{y} NPs have little chiroptical activity in the UV-visible range (dotted lines, Figure 4.6e), probably due to the small nominal P of 5 nm. The coating of Al (Figure 4.6c, d), as confirmed by XPS (Figure 4.7c), causes a markedly chiroptical activation in a $\lambda$ range of 200 – 700 nm (solid lines, Figure 4.6e). The $g$-spectrum of the Fe\textsubscript{x}O\textsubscript{y} NPs@Al appears to be nearly symmetric around the zero-$g$ axis, while the hidden handedness of the non-plasmonic host is switched (Figure 4.6f). On the contrary, there is nearly no chiroptical induction while coating Al on the host of achiral Fe\textsubscript{x}O\textsubscript{y} NPs (black lines, Figure 4.6e, f). It can be deduced that the Al nanocappings tend to duplicate the hidden helical structures of the underneath host, such that the helicity duplication makes an essential contribution to the chirality transfer from the chiral host to achiral guest.
Figure 4.7 XPS spectra of (a, b) LH-Fe\textsubscript{x}O\textsubscript{y}NPs (with a \textit{P} of 5 and \textit{H} of 40 nm) and (c) LH-Fe\textsubscript{x}O\textsubscript{y}NPs@Al: (a) Fe\textsubscript{2p}, (b) O\textsubscript{1s}, and (c) Al\textsubscript{2p}.

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.

4.2 Conclusion

We devise two GLAD-related methods to generate chiral Al nanostructures with chiroptical response in the UV-visible region, in which the Al nanostructures can be quickly deposited to avoid short circuit that usually occurs in a long-duration evaporation of Al due to low melting point of Al. One approach involves the fast rotation of substrate during GLAD to fabricate AlNPs with hidden helicity; another is to deposit Al onto the host of chiral plasmonic NPs, such that the structural helicity are duplicated from the chiral host to the achiral guest of Al nanocappings. The host@guest helicity duplication can be generally adapted to diverse plasmonic materials. The chiral Al nanostructures have crystalline structures, undergo native oxidation under ambient conditions, and exhibit stable chiroptical activity in the UV-visible region that originates from the intrinsic helical structures. Chiroptical activity of the chiral AlNPs is stronger than the induced chiroptical response of the Al nanocappings, due to the partial guest coating on the host and consequently the partial helicity transfer. The achiral guest can amplify the chiroptical activity of the chiral host.
Chapter 5 Enantioselective Photocyclodimerization of 2-Anthracenecarboxylate on Plasmonic Nanohelices

The generation and manipulation of molecular chirality is undoubtedly among the most important topics in modern chemistry. A pair of enantiomeric compounds, being mutual non-superimposable mirror reflections, is known to have essentially the same generation of free energy from prochiral precursors and should commonly be formed with equal probability. Practically, most artificial enantiomeric enrichment and purification are obtained by enantiodifferentiating reactions or resolutions mediated with chiral molecules. In contrast, biosystems show startling homochiral properties, as revealed by the exclusive existence of biologically relevant molecules as one of the two enantiomers, such as L-amino acids and D-sugars. The biological homochirality raised the question of the mystical origin of the initial molecular enantio-preference on the earth. Several intriguing chiral phenomena, such as spontaneous symmetry breaking, chirality amplification, and asymmetric autocatalysis, are relevant to this issue. Efforts have been devoted to explore the external physical factors, including CPL and magnetic fields, to achieve enantiomeric enrichment in the absence of any chiral matter.

Macroscopic chiral operations, such as vortex and stirring, have demonstrated the ability to generate chirality of supramolecular aggregates. However, manipulation of molecular chirality via such operations is evidently challenging and demands a chirality transfer of visible macroscopic behavior to a size as small as the sub-nanometer scale.

With the collaboration of Prof. Cheng Yang at Sichuan University, photocyclodimerization of AC has been extensively studied as a model photoreaction for evaluation of the photochirogenic abilities of chiral supramolecular systems. Photoirradiation of AC leads to the formation of four [4 + 4] regioisomers 1-4 (scheme 5.1), of which syn-head-to-tail (syn-HT) dimer 2 and
anti-head-to-head (anti-HH) dimer 3 are chiral. In this article, we report the photochirogenic dimerization of AC on the surface of nanohelices, formed via macroscopic rotation, in the absence of any chiral molecule.


5.1 Results and discussion

One-pitch AgNHs were deposited by GLAD on periodic seeds; these have left and right handedness (i.e., LH-AgNHs [Figure 5.1a, c] and RH-AgNHs [Figure 5.1b]). AgNHs have a helical pitch ($P$) of approximately 150 nm and crystalline structures (Figure 5.1d, e) and are spontaneously oxidized (Figure 5.1f). The substrate temperature ($T_{\text{sub}}$) was controlled to be approximately −40°C, almost the lowest $T_{\text{sub}}$. 
obtained using our GLAD equipment. Such a \( T_{\text{sub}} \) cannot sufficiently prohibit the surface diffusion of Ag adatoms on the deposited Ag nanostructures, and the sculptured AgNHs appear not to have a helical profile as well-defined as those deposited at \( T_{\text{sub}} \) of approximately \(-190^\circ\text{C}\) (controlled with liquid nitrogen).

Figure 5.1 GLAD of periodic arrays of one-pitch AgNHs with a helical pitch (\( P \)) of approximately 150 nm: (a) left-handed (LH-AgNHs), (b) right-handed (RH-AgNHs). (a, b) Cross-sectional SEM images. TEM images of LH-AgNH: (c) low resolution, (d) high resolution. (e) XRD and (f) XPS spectrum of natively oxidized LH-AgNHs. Note that RH-AgNHs have analogous XRD and XPS spectra.

To mediate AC photocyclodimerization, however, the AgNHs were deposited on a flat substrate to generate a close-packed random array for two reasons. The first reason is that the periodic patterns are composed of polymer, which would contaminate the photocyclodimerization. The other reason is that given an area of
a substrate, the close-packed array with a high surface density of AgNHs can produce a sufficient amount of photocyclodimerization products for HPLC characterization, but the periodic array with a lower surface density cannot.

**Figure 5.2** UV–visible spectra of AgNHs with a helical pitch (P) of approximately 220 nm (a, b) and 130 nm (c, d): (a, c) extinction; (b, d) CD; LH (red lines); RH (blue lines).

**Figure 5.3** Adsorption of AC on AgNHs with a P of 53 nm. Raman spectra: (a) AC powders, (b) LH-AgNHs grafted with AC, (c) pristine LH-AgNHs. The peak at 754 cm$^{-1}$ is assigned to the skeletal (anthracene) stretching of AC, and the peaks at 1408 and 1556 cm$^{-1}$ are assigned to the aromatic C=C stretching of AC. UV–visible spectra of (d) extinction and (e) CD (measured with a J-1500 CD spectrometer): LH (red lines), RH (blue lines), AgNHs without (dotted lines) and with (solid lines) adsorption of AC. Inset in (d): extinction spectra of RH-AgNHs without (dotted lines) and with (solid lines) adsorption of AC, in a wavelength range of 350 to 380 nm.

The close-packed random arrays of AgNHs with a P of approximately 220 nm (Figure 5.2a-b), 130 nm (Figure 5.2c-d), 50 nm (Figure 5.3a-b), and 8 nm (Figure 5.3d-e) exhibit CD spectra that flip around the zero-CD axis while switching the handedness of the AgNHs, illustrating that the AgNHs have UV–visible chiroptical
activity that originates intrinsically from their helicity. The chiroptical response of the AgNHs is composed of the transverse (T) and longitudinal (L) LSPR/resonant CD modes at a wavelength of approximately 365 nm and in the visible region, respectively. Note that the 8-nm-pitch AgNHs appear to be vertical nanorods (inset in Figure 5.4d-e) because they have a wire diameter \( d \) greater than \( P \). AC absorbs UV light and exhibits a broad absorption peak centered at a wavelength of approximately 365 nm (green line, Figure 5.4a-b and 5.4d-e), resonant with the T-LSPR/CD mode of the AgNHs. Under non-polarized 365-nm irradiation, the photocyclodimerization of AC was resonantly mediated on the AgNHs. This leads to generation of the chiral anti-HH cyclodimer 3 and achiral syn-HH cyclodimer 4, characterized by HPLC (Figure 5.4c). There is no production of the HT cyclodimers 1 or 2, in that two AC molecules of a dimer preferentially have undergone simultaneous grafting on the AgNHs by forming Ag-OOC bonds. The surface grafting of AC can be confirmed by detecting the skeletal stretching of AC at 754 cm\(^{-1}\) in the Raman spectrum (Figure 5.3a-c) and by monitoring a slight red-shift and chiroptical weakening of the T-mode (Figure 5.3d, e) attributed to the AC grafting-induced increase of the medium dielectric constant. For the chiral anti-HH cyclodimer 3, the enantiomeric excess (ee) can be calculated by

\[
\text{ee} = \frac{I_{3,+} - I_{3,-}}{I_{3,+} + \cdot I_{3,-}} \times 100\% \quad (5.1)
\]

where \( I_{3,+} \) and \( I_{3,-} \) are the HPLC peak intensity of the enantiomer (+)-3 and (−)-3, respectively. Intriguingly, the photocyclodimerization of AC mediated on the AgNHs with left/right handedness generally gives rise to a positive/negative ee value of the anti-HH cyclodimer 3, in a \( P \) range of 7 to 235 nm (Figure 5.5a). Without the helical handedness, tilted silver nanorods fabricated by GLAD (inset in Figure 5.4h-i) are chiroptically inactive in the UV-visible region (Figure 5.4i), resulting in the production of a racemic mixture of (+)-3 and (−)-3 with a negligible ee value (Figure 5.4j). It is clearly illustrated that the chiral handedness of the
AgNHs plays an essential role in enantioselective photocyclodimerization. The average $ee$ value tends to decrease from approximately 5% to approximately 2% with an increase of $P$ from 7 to 235 nm and roughly flips in sign around the zero-$ee$ axis while switching helical handedness (Figure 5.5b). The $ee$ value generally has a relatively large standard deviation, probably because the close-packed random AgNH arrays tend to have a wide distribution of helical structures and random structural defects.

Figure 5.4 Photocyclodimerization of AC on (a-c) AgNHs with a $P$ of approximately 50 nm; (d, e) AgNHs with a $P$ of approximately 8 nm and a height ($H$) of approximately 250 nm; (f, g) CuNHs with a $P$ of approximately 65 nm; (h-j) titled Ag nanorods: LH (red lines), RH (blue lines), Ag nanorods (black lines). UV–visible spectra: (a, d, f, h) extinction (i.e., Ext); (b, e, g, i) CD. (c, j) HPLC chromatograms. Insets: (a) absorption spectrum of ethanol dissolved with 0.2 mmol/L AC (olive line); (a, b, d-g) vertical olive dashed lines represent the non-polarized irradiation with a wavelength of 365 nm; cross-sectional SEM images of (d, e) vertical LH-AgNHs with a $P$ of approximately 8 nm and (h, i) tilted Ag nanorods; (c, j) HPLC chromatograms of the chiral anti-HH cyclodimer (+)-3 and (-)-3. (a, b, d-g) Chiral LSPR of plasmonic NHs is marked by the pink background.

The enantioselective photocyclodimerization associated with the helical handedness of the AgNHs is probably ascribed to two mechanisms, chirally helical surface-induced enantioselective adsorption of AC dimers and chiroptically active nanoplasmon-enhanced optical chirality of CPL. According to the adsorption-induced chirality, on an achiral surface of, for example, tilted silver nanorods,
the \textit{anti-HH} dimers adsorb in one absolute configuration at the same probability as in its mirror image, resulting in a non-enantioselective photocyclodimerization. The AgNHs provide the chirally helical surfaces to break the mirror symmetry of the \textit{anti-HH} dimer adsorption: \footnote{146} LH-AgNHs cause a preference of the dimer adsorption in one absolute configuration, and RH-AgNHs have a preference in another. Such an asymmetric dimer adsorption induced by the chirally helical surfaces gives rise to enantioselective photocyclodimerization. For the second mechanism, non-polarized 365-nm light is incident to resonantly excite chiroptically active nanoplasmons from the AgNHs at the LSPR wavelength of approximately 370 nm, resulting in an effective amplification of the optical chirality of electromagnetic near fields on the helical surfaces \footnote{14} at the resonant frequency at which the absorption of AC occurs to trigger photocyclodimerization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5.5.png}
\caption{\textit{ee} values of the chiral product 3 of the photocyclodimerization on plasmonic NHs, under non-polarized irradiation with a wavelength of 365 nm. (a) Columnar distribution of \textit{ee} values as a function of \textit{P} (as described in the plot): LH (red columns), RH (blue columns), AgNHs (white background), CuNHs (pink background). (b) Plot of \textit{ee} values as a function of \textit{P}: LH (red squares), RH (blue squares), AgNHs (solid squares), and CuNHs (empty squares).}
\end{figure}

The optical chirality (represented by \textit{C}), which has a positive or negative sign to represent different circular polarization states of CPL (i.e., LCP and RCP), describes the degree of chiral asymmetry in the rate of excitation of enantiomers. \footnote{12} A large \textit{C} with a positive or negative sign is favored for light absorption of the \textit{anti-HH} dimers that have one absolute configuration or another, accounting for the
enantioselective photocyclodimerization. The two mechanisms tend to make synergistic contributions to enantioselective photocyclodimerization: the AgNHs with a given handedness give rise to the enantioselective adsorption of the anti-HH dimers and cause asymmetric amplification of the near-field optical chirality of a circular polarization state (LCP or RCP) that will be absorbed by the enantiomeric dimers enantioselectively adsorbed on the AgNHs with the given handedness.

Figure 5.6 UV–visible spectra of CuNHs with a helical pitch ($P$) of approximately 8 nm (a, b), approximately 130 nm (c, d) and approximately 250 nm (e, f): (a, c, e) extinction; (b, d, f) CD; LH (red lines); RH (blue lines).

To solely study the chirally helical surface-induced mechanism, the AC photocyclodimerization was mediated on one-pitch NHs made of non-plasmonic materials under 365-nm non-polarized irradiation, that is, copper with a plasmonic frequency of greater than 600 nm. Under UV irradiation, Cu has a larger extinction coefficient than that at the plasmonic frequency, so that plasmons cannot be effectively excited and Cu turns to be dielectric. Analogous to the helical structures of the AgNHs, copper NHs (CuNHs) were deposited by GLAD to have a $P$ engineerable in a range of 8 to 225 nm, exhibiting LSPR and resonant CD at a wavelength longer than 550 nm (Figure 5.4f, 5.4g, and 5.6). The anti-HH dimers can adsorb on the CuNHs by forming Cu-OOC contacts. However, the dimer adsorption could hardly be monitored by Raman spectroscopy because the CuNHs could not effectively enhance Raman scattering of the self-assembled dimers.

Intriguingly, the CuNHs mediate the enantioselective photocyclodimerization of AC in a manner analogous to that of the AgNHs: the left/right handedness causes
positive/negative ee values (Figure 5.5a). Given that no plasmon excited on the CuNHs at the UV frequency, it is illuminated that the helical surface–induced enantioselective dimer adsorption plays an essential role in the enantioselectivity. Statistical analysis was performed to show that the dielectric CuNHs cause the average enantioselectivity to decrease with increasing $P$ (empty symbols, Figure 5.5b). It is illustrated that a small $P$ is favored to cause enantioselective adsorption of the anti-HH dimers owing to the dimensional matching between the dimers and $P$. Furthermore, the dielectric CuNHs give rise to an average ee value lower than the plasmonic AgNHs in the $P$ range of 7 to 230 nm (empty versus solid symbols, Figure 5.5b). Given that bond energy of Cu-OOC is simulated to be larger than that of Ag-OOC,\textsuperscript{143} it is indicated that there is an additional contribution, that is, chiroptically active nanoplasmons excited from the AgNHs, to enhance enantioselective photocyclodimerization.

Figure 5.7 (a) Schematic of simulated optical chirality $C$ on a LH-AgNH (with a $d$ of 56 nm, $D$ of 186 nm, $H$ of 182 nm, $n$ of 1, $P$ of 126 nm), under linearly polarized irradiation with a wavelength of 365 nm. The azimuthal angle $\phi$ is the angle between the linearly polarized electric field and the positive direction of $x$-axis. (b) Simulation results of the ee values as a function of $\phi$: LH-AgNH (red squares), RH-AgNH (blue squares), solid lines represent the sinusoidal variation of ee with $\phi$. The red and blue dashed lines represent the average ee value of 19.32% for the LH-AgNH and $-19.32\%$ for RH-AgNH. The simulated AgNH has a $P$ of 126 nm. (c) Simulation results of the $\phi$-averaged ee values of a LH-AgNH as a function of $P$ and the distance from the AgNH surface: 0.5 nm (red hollow circles), 1 nm (black hollow circles), and 2 nm (blue hollow circles).

To understand the contribution of chiroptically active nanoplasmons, the finite-element method\textsuperscript{41,43} was used to numerically simulate $C$ of the electromagnetic near field on the helical surfaces of an AgNH (Figure 5.7) under non-polarized 365-nm
irradiation (completed by Dr. Deng Junhong in HKBU). The non-polarized incidence was simulated by averaging the linearly polarized irradiation over the azimuthal angle $\phi$ (i.e., the angle between the linearly polarized electric field and the positive direction of x-axis, Figure 5.7a) between 0° and 165° at intervals of 15°. For instance, the 365-nm linearly polarized irradiation was numerically simulated on a LH-AgNH with a $P$ of 126 nm at a given $\phi$ (Figure 5.7a). The simulation reveals that the LH-AgNH surface exhibits a variance of localized $C$ in magnitude and sign, especially at the locations with high surface curvatures. The sign of $C$ denotes the circular polarization state of CPL; a positive sign represents LCP (when an observer is facing an oncoming LCP, the rotation of the electric field is anticlockwise) and a negative sign denotes RCP (the rotation of the electric field is clockwise when looking into an RCP). For example, the LH-AgNH exhibits alternate LCP and RCP with large $C$ at the both ends. The localized $C$ varies in magnitude and sign because the linearly polarized light is composed of LCP and RCP, and the chirality-dependent interaction of the AgNH and light has a marked effect on the localized $C$ on the helical surfaces.\textsuperscript{14} The photocyclodimerization enantioselectivity will be intrinsically determined by the chirality-dependent interaction of CPL and the anti-HH dimers, both of which have spatial distribution of chirality on the helical surfaces. Although the spatial distribution of the enantiomeric chirality of the anti-HH dimers is unknown, an excess of one enantiomeric chirality will be obtained on the surface of the LH-AgNH. The excess of $C$ ($e_C$) can be calculated by

$$
e_C = \frac{|\sum C_{i,+}| - |\sum C_{i,-}|}{|\sum C_{i,+}| + |\sum C_{i,-}|} \times 100\% \quad (5.2)$$

where $C_{i,+}/C_{i,-}$ denotes the simulated value of $C$ with a positive/negative sign at each intersection in the meshes into which the surface of the LH-AgNH is divided. Given the excess of one enantiomeric chirality of the anti-HH dimers, a large $e_C$ is favored for enantioselective photocyclodimerization.
To simulate photocyclodimerization under non-polarized irradiation, the $e_C$ value was calculated as a function of $\phi$ in the range of 0° to 165°, with an interval of 15°. The $e_C$ value under the linear polarization irradiation varies sinusoidally with $\phi$ (Figure 5.7b), and the $\phi$-averaged value represents the $e_C$ value under non-polarized irradiation (marked by dashed lines in Figure 5.7b). The numerical simulation reveals that, given a helical structure, LH-AgNH and RH-AgNH have identical $e_C$ values with opposite signs. It is illustrated that the helical handedness of the AgNHs substantially determines the net circularly polarized state of the electromagnetic near field on the helical surface. Due to the helicity-associated symmetry of the $\phi$-averaged $e_C$ values, it is only shown the $\phi$-averaged $e_C$ values of a LH-AgNH as a function of $P$ in Figure 5.7c. The numerical simulation was performed as a function of a distance from the helical surface between 0.5 and 2 nm, in which the adsorbed anti-$HH$ dimers can effectively interact with the scattered CPL. It is determined that the $e_C$ values have a negligible dependence on the distance, and the $\phi$-averaged $e_C$ value tends to decline with an increase of $P$. It can be derived from the synergistic contribution of the two mechanisms that a small $P$ of the AgNHs is favored to induce the enantioselective adsorption of the anti-$HH$ dimers and the asymmetric amplification of the near-field circularly polarized state, leading to enhancement of the enantioselective photocyclodimerization.

5.2 Conclusions

Plasmonic NHs can mediate the photocyclodimerization of AC under 365-nm non-polarized irradiation. The helical handedness determines the enantioselectivity of the anti-$HH$ cyclodimers: the left/right handedness of the AgNHs gives rise to an $ee$ value with a positive/negative sign. The AgNH-mediated enantioselective photocyclodimerization can be ascribed to the synergistic contribution from the chirally helical surface-induced enantioselective adsorption of the anti-$HH$ dimers and the chiroptically active nanoplasmon-enhanced optical chirality of CPL.
Chapter 6 Reducing the porosity and reflection loss of silicon nanowires by a sticky tape

Mmp-SiNWs can be created via metal-assisted chemical etching (MACE) of Si wafers, and it has been reported that the porosity increases with the concentration of etchants (e.g. HF), the concentration of oxidizers (e.g. H₂O₂), etching duration, doping level of Si wafers, etching temperature, and etching current.

This work introduces a new method to alter the porosity of mp-SiNWs with no change in MACE conditions. MACE is operated twice on a heavily doped n-Si(100) (i.e., Bi-MACE). The first MACE generates mp-SiNWs, which are taped off with sticky tape. Then the taped wafer is treated by MACE a second time to fabricate mp-SiNWs. A systematic comparison is made to illustrate that the first MACE produces mp-SiNWs that are more porous than those produced by the second MACE. We also studied how the porosity of mp-SiNWs affects reflection loss in the ultraviolet (UV)-visible range, and why Bi-MACE decreases the porosity of mp-SiNWs.

6.1 Results and discussion

6.1.1 Bi-MACE

The first MACE creates vertical SiNWs that protrude on a layer of mesoporous Si (mpSi, Figure 6.1a), and the SiNWs appear to be mesoporous (Figure 6.2a). The as-generated mp-SiNWs are transferred to a 3M sticky tape via mechanically taping off (Figure 6.1a), leaving broken mp-SiNWs and the intact mpSi layer on the wafer (Figure 6.1c). Then MACE is repeated on the taped wafer to generate vertical SiNWs (Figure 6.1d). There are some significant differences in the mp-SiNWs produced by the first and second MACE treatments. For one, the first MACE generates mp-SiNWs that are much shorter than those generated by the second
MACE within the same period of time (i.e., 3.4 μm, as seen in Figure 6.1a, versus 8 μm, as seen in Figure 6.1d). Also, the second MACE makes the wafer appear to be much darker than the first MACE (compare the insets, Figures 6.1a and 6.1d).

Figure 6.1 Bi-MACE of n⁺²-Si(100). (a) The 1st-MACE lasting for 1 hr to generate mp-SiNWs with higher porosity (mpʰ-SiNWs). (b) mpʰ-SiNWs are transferred to a 3M tape. (c) The residue left on n⁺²-Si(100) after the transfer of mpʰ-SiNWs. (d) The 2nd-MACE lasting for 1 hr to create mp-SiNWs with lower porosity (mpˡ-SiNWs). SEM images with side-viewing (a), top-down viewing (b) and oblique viewing (c, d). Insets: photographs of n⁺²-Si(100) after the 1st-MACE (a), a 3M tape with transferred mpʰ-SiNWs (b), and n⁺²-Si(100) after the 2nd-MACE (d); a SEM oblique image magnifying the area that is highlighted by a red box.

In addition, the first MACE creates mp-SiNWs that aggregate in the upper portions, which isn’t observed after the second MACE. Finally, the first MACE produces mp-SiNWs with higher porosity than those generated by the second MACE (compare Figure 6.2a and 6.2b). Herein, it is denoted that mpʰ-SiNWs with high porosity are produced by the first MACE, and mpˡ-SiNWs with low porosity are produced by the second MACE.
This difference in porosity can be further demonstrated. First, SEM shows that mp\textsuperscript{H}-SiNWs appear to be blurrier than mp\textsuperscript{L}-SiNWs (compare Figure 6.2c and 6.2d). This is attributed to the fact that porous nanostructures tend to scatter incident electrons in diverse directions, and the scattering becomes severe with the increasing porosity of the mp-SiNWs. Second, mp\textsuperscript{H}-SiNWs are mechanically weaker than mp\textsuperscript{L}-SiNWs\textsuperscript{113}. While drying the wet-etched wafers, the evaporation of water applies strong capillary force to mp-SiNWs. mp\textsuperscript{H}-SiNWs with weak mechanical strength tend to aggregate in the upper sections (Figure 6.1a). Sometimes mp\textsuperscript{H}-SiNWs are mechanically weak enough to cluster together (Figure 6.3a). On the contrary, mp\textsuperscript{L}-SiNWs are mechanically too strong to aggregate against the capillary force (Figure 6.1d), analogous to solid SiNWs without pores\textsuperscript{86}. Furthermore, low mechanical strength makes mp\textsuperscript{H}-SiNWs easily taped off the Si wafers. The inset in Figure 6.1(b) shows that mp\textsuperscript{H}-SiNWs can easily be uniformly transferred to a tape in an area of 0.75 \times 1.5 \text{ cm}^2. However, it is very difficult to tape off mp\textsuperscript{L}-SiNWs. Third, it was recently reported that 40% aqueous NH\textsubscript{4}F solution can etch SiNW(100), which is
ascribed to the nucleophilic attack of F- anions on Si atoms; the etching rate increases with the porosity of SiNW(100)\textsuperscript{148}. Bi-MACE generates mp-SiNW(100) due to the vertical protrusion on n+2-Si(100)\textsuperscript{17,18}. Within 2 min, 40% NH\textsubscript{4}F almost completely etches mp\textsuperscript{H}-SiNWs (Figure 6.3(b)), but mp\textsuperscript{L}-SiNWs remain mostly intact after this time (Figure 6.3(d)), illuminating the fact that mp\textsuperscript{H}-SiNWs have higher porosity than mp\textsuperscript{L}-SiNWs. Fourth, under UV excitation (325 nm), mp-SiNWs emit a reddish PL centered at \( \sim 690 \) nm, regardless of the porosity (Figure 6.4). Compared to mp\textsuperscript{H}-SiNWs, mp\textsuperscript{L}-SiNWs emit weaker PL with a slight red shift. The reddish PL originates from the oxide/Si interfacial states, instead of the porosification-induced quantum confinement. mp\textsuperscript{H}-SiNWs are more porous, and hence contain more interfacial states than mp\textsuperscript{L}-SiNWs, accounting for the stronger emission of reddish PL. The slight red shift may be attributed to the difference in the interfacial states on mp\textsuperscript{H}-SiNWs and mp\textsuperscript{L}-SiNWs.

### 6.1.2 Antireflection

The wafer covered with upper-aggregating mp\textsuperscript{H}-SiNWs appears to be brown under reflection (the inset in Figure 6.1a), and becomes brighter with the clustering (the inset in Figure 6.3a). mp\textsuperscript{L}-SiNWs significantly darken the wafer (the inset in Figure 6.1d indicating strong antireflection. The antireflection is characterized by specular reflection at an incident angle of 30° with respect to the substrate normal (Figure 6.5). The darker the wafer, the lower the specular p- and s-polarized reflection in the broadband of 300–800 nm. Light can be trapped via multiple reflections from neighboring NWs that vertically protrude on surfaces\textsuperscript{149}, leading to antireflection. The elongation of NWs without clustering can enhance optical trapping. mp\textsuperscript{L}-SiNWs are longer than mp\textsuperscript{H}-SiNWs and nearly eliminate the aggregation, thus reducing reflection loss. Furthermore, optical scattering from the porous, non-smooth surfaces can deteriorate antireflection. mp\textsuperscript{L}-SiNWs are less porous than mp\textsuperscript{H}-SiNWs; the lower level of porosity further reduces reflection loss\textsuperscript{113}. 

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Figure 6.3 mpH-SiNWs (a, b) and mpL-SiNWs (c, d) exposed in 40% aqueous NH4F for 0 (a, c) and 2 min (b, d). SEM images: (a, b) oblique viewing, and (c, d) side-viewing. Insets in (a): down-left is a photograph of mpH-SiNWs protruding on a n$^+$-Si(100), and upper-right is a SEM cross-sectional image.

6.1.3 Bi-MACE mechanism

MACE is an anisotropically galvanic etching $^{78}$, given by $^{80}$

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag(s)} \quad \text{(eq. 6.1)} \]
\[ \text{Si(s)} + 2\text{H}_2\text{O} - 4e^- \rightarrow \text{SiO}_2 \text{(s)} + 4\text{H}^+ \quad \text{eq. 6.2) } \]
\[ \text{SiO}_2 \text{(s)} + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \quad \text{(eq. 6.3)} \]

Ag$^+$ ions nucleate on the wafer surfaces via equation (6.1), driven by the oxidation of Si underneath the nuclei (equation (6.2)). HF dissolves the oxidized SiO$_2$ (equation (6.3)) and creates pits to trap Ag nuclei. Equation (6.2) generates four electrons, but equation (6.1) consumes only one electron at a time. The excess electrons migrate from the wafer and accumulate on the nuclear surfaces to electrostatically drive Ag$^+$ cations toward the nuclei for reduction (equation (6.1)). Then equations (6.1) – (6.3) repeatedly take place to drive Ag nuclei to continuously
etch the Si, sink into the wafer, and simultaneously grow into dendrites on the wafer surface. After the removal of Ag particles by HNO₃, the scratched portions of the wafer appear to be an array of SiNWs without pores. The etching is catalyzed by Ag particles, through which electrons transport from Si to the Ag/electrolyte interfaces. Note that the nucleation preferentially occurs at surface states, such as dangling bonds, structural defects (steps, kink sites, and dislocations), and sites around the dopants. n⁺²-Si(100) is heavily doped to provide enormous nucleation sites, so that large amounts of Ag⁺ cations nucleate on the surface to significantly reduce [Ag⁺] (i.e., the concentration of Ag⁺ cations) in the electrolyte. Low [Ag⁺] can support only a portion of the Ag nuclei to grow and continuously sink into the wafer. The rest of the non-grown Ag nuclei undergo a random, transient scratching to porosify the as-generated SiNWs and the bulk Si underneath, leading to the generation of a hybrid structure that mp-SiNWs protrude on mpSi (Figure 6.1a).

Figure 6.4 Ambient PL spectra of mp⁺²-SiNWs (Fig. 6.1a) and mp⁺¹-SiNWs (Fig. 6.1d). The system noise is marked by asterisk.
Figure 6.5 UV-visible specular reflection spectra of the arrays of mp\textsuperscript{H}-SiNWs (Fig. 16a and 18a) and mp\textsuperscript{L}-SiNWs (Fig. 16d), at an incident angle of 30° with respect to the substrate normal. (a) p-polarization, and (b) s-polarization.

Figure 6.6 Bi-MACE of n\textsuperscript{+2}-Si(100) without dissolving Ag dendrites. (a), (c) The 1\textsuperscript{st}-MACE lasting for 5 min; (b), (d) the 2\textsuperscript{nd}-MACE lasting for 5 min. SEM images: (a, b) top-down views; (c, d) oblique views.

The first MACE is operated on a smooth surface, but the sticky tape makes the second MACE occur on a rough surface composed of broken SiNWs and a thick mpSi layer (Figure 6.1a). Why can the pretaping effectively alter the porosity of SiNWs without changing the MACE conditions? The evolution of the second MACE (Figure 6.7) illustrates that the taping-caused residues are gradually etched...
before generating mpL-SiNWs. Three factors may account for the fabrication of mpL-SiNWs. First, the pre-etching of the residues significantly reduces [HF] and [Ag⁺]. The MACE of a smooth n⁺²-Si (100) is systematically mimicked at [HF] and [Ag⁺], which are lower than those used in the Bi-MACE (Figure 6.8).

**Figure 6.7** The evolution of the 2nd-MACE of n⁺²-Si(100), lasting for (a) 1 min; (b) 5 min; (c) 10 min; (d) 20 min. SEM images: (a, b) oblique viewing, (c, d) side viewing. Insets: the top right of (a) and top left of (b) are SEM oblique-viewing images of other spots of the samples; the other four are the photographs of the as-etched wafers with the etching evolution.

SiNWs produced by the low-concentration MACE appear to be much shorter than those generated by the second MACE within the same period of time (i.e., 1 h), and they aren’t intact in 40% NH₄F, indicating the fabrication of mp⁺H-SiNWs instead of mp⁺L-SiNWs. It is understood that the second MACE cannot be attributed to the decrease of [HF] and [Ag⁺]. Second, we consider the crystallinity of Ag dendrite catalysts. Electrons donated by the oxidation of Si (equation (6.2)) migrate through Ag dendrites to the Ag/electrolyte interfaces, and the electron transport is affected by the crystallinity of the Ag dendrites. However, both the first and second MACE generate polycrystalline Ag dendrites with indistinguishable mean crystalline sizes
(Figure 6.9 and Table 6.1), excluding the contribution of dendrite crystallinity to the second MACE.

The scherrer's equation is customary used to estimate the mean crystallite size, given by,

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where $\tau$ is the mean size of the domain crystalline; $K$ is a dimensionless shape factor varying with the actual shape of the crystallite; $\lambda$ is the X-ray wavelength; $\beta$ is the line broadening at half the maximum intensity (FWHM); $\theta$ is the Bragg angle.

We calculated the ratio of $\tau$ between Ag dendrite on surface of mp$^H$-SiNWs and mp$^L$-SiNWs arrays, $\frac{\tau_H}{\tau_L}$ is 0.983. It meant that there was no much crystalline difference of Ag dendrite formed during 1$^{st}$- and 2$^{nd}$-MACE process. So the crystalline was not the determinate factor of the porosity diversity.

Third, the taping-caused residues have mesoporous structures that are more chemically active than the bare Si surfaces. It is deduced that the second MACE generates Ag dendrites at a faster rate than the first MACE, which is demonstrated in Figure 6.6. At the beginning of etching (e.g., within the first 6 min), the second MACE creates Ag dendrites thicker than those created by the first MACE (Figure 6.6b versus 6.6a, Figure 6.6d versus 6.6c). The thickening of Ag dendrites that cover the wafer tends to prohibit Ag$^+$ cations from diffusing to and porosifying the bulk Si underneath, and it facilitates the condensation of Ag$^+$ cations on the dendrites. Consequently, the growth of Ag dendrites is preferential over the Si porosification, which accounts for the decrease of the SiNWs’ porosity in the second MACE. The preference in the dendrite growth can also explain that mp$^L$-SiNWs are longer than mp$^H$-SiNWs, since the growth of Ag dendrites is mainly accompanied with the vertical scratching of growing Ag particles on the wafer.
**Figure 6.8** The 1\textsuperscript{st}-MACE of n\textsuperscript{+2}-Si(100) lasting for 1 hour: (a) [HF] of 2.4 mol/L and [AgNO\textsubscript{3}] of 0.01 mol/L; (b) [HF] of 2.4 mol/L and [AgNO\textsubscript{3}] of 0.005 mol/L; (c) [HF] of 1.2 mol/L and [AgNO\textsubscript{3}] of 0.01 mol/L; (d) [HF] of 0.6 mol/L and [AgNO\textsubscript{3}] of 0.01 mol/L. The as-generated mp\textsuperscript{+1}-SiNWs (a-d) are dipped in 40% aqueous NH\textsubscript{4}F solution for 2 min (e-h). (a-h) SEM oblique images, with a scale bar of 1\,\mu m.

**Table 6.1** The calculation of $\tau$ in terms of Ag(111), It is assumed that K of Ag dendrites is independent on the MACE process.
<table>
<thead>
<tr>
<th>Ag dendrites</th>
<th>$2\theta$</th>
<th>$\beta$</th>
<th>$\tau_{1st}/\tau_{2nd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>The 1st-MACE</td>
<td>38.1327</td>
<td>0.2104</td>
<td></td>
</tr>
<tr>
<td>The 2nd-MACE</td>
<td>38.1367</td>
<td>0.2073</td>
<td>0.9851</td>
</tr>
</tbody>
</table>

**Figure 6.9** XRD spectra of Ag dendrites formed on the surfaces of mp$^\text{H}$-SiNWs and mp$^\text{L}$-SiNWs. The inset magnifies the Ag(111) XRD peaks.

**6.2 Conclusion**

The first MACE of $n^{+2}$-Si(100) creates mp$^\text{H}$-SiNWs. mp$^\text{H}$-SiNWs are transferred from the wafer to a sticky tape, leaving residues composed of broken mp$^\text{H}$-SiNWs and an mpSi layer on the wafer. Then the taped wafer is treated by the second MACE, with no change in MACE conditions. Before creating mp-SiNWs, the residues are first electrochemically etched to generate Ag dendrites. The mesoporous residues are more chemically active than the smooth wafer exposed to the first MACE, so that the second MACE generates Ag dendrites at a faster rate than the first MACE. The thickening of Ag dendrites effectively blocks the diffusion of Ag$^+$ cations to the bulk Si underneath, thus prohibiting the porosification and generating mp$^\text{L}$-SiNWs at a faster rate than the first MACE.
Compared to mp$^\text{H}$-SiNWs, mp$^\text{L}$-SiNWs have higher mechanical strength, allowing them to protrude vertically without the aggregation at the upper portions. mp$^\text{L}$-SiNWs have less reflection loss than mp$^\text{H}$-SiNWs in the broadband of 300–800 nm, since the nonaggregating array of long mp$^\text{L}$-SiNWs facilitates optical trapping and low porosity in mp$^\text{L}$-SiNWs suppresses optical scattering from the porous Si skeletons. This work contributes to generating a new approach to engineer the porosity of SiNWs, which is of fundamental and technical interest in SiNW-based devices to modify the performance of PL, nanoelectronics, optoelectronics, energy storage and generation, molecular sensing, and drug delivery. This work has been published in *Nanotechnology* (2015, 26, 185601). ¹⁵⁰
Chapter 7 Anion F⁻- Induced Etching of Silicon Nanowires with Diverse Doping Levels, Surface Crystalline Orientations, and Porosity

There are mainly three approaches developed for surface modification on Si, including the hydrosilylation of H-terminated Si (i.e., H:Si), two-step chlorination/alkylation of H:Si, and the silanization of oxide-covered Si. It is a prerequisite in the first two methods to generate H:Si surfaces. It has been well studied that dilute aqueous HF can generate H:Si(100) with nanometer scale roughness, and 40% aqueous NH₄F can create H:Si(111) with atomic flat surfaces. Analogously, dilute aqueous HF can graft H onto SiNWs, which have diverse surface crystalline orientations (i.e., (100) and (111)) and porosity (i.e., solid and mesoporous SiNWs). However, Chen et al. reported that aqueous NH₄F does eventually dissolve SiNWs. They ascribed the dissolution to surface termination with −OH instead of −H, but did not provide any spectral evidence to confirm the OH-termination. They fabricated an intersecting network of solid SiNWs with unknown mass, number, and length of NWs so that the etching dynamics could only be studied by monitoring the duration of complete dissolution of the SiNW network. The dynamic analysis was short of quantitative information.

In this work it will be fabricated an array of SiNWs vertically protruding on a Si wafer by means of metal-assisted chemical etching (MACE), and quantitatively evaluate the etching rate of SiNWs in 40% aqueous NH₄F with respect to the NW-length shrinkage. A series of spectral characterization experiments will be carried out to confirm that the surfaces are F-terminated rather than OH-terminated. An etching mechanism will be proposed to account for the NH₄F etching induced by the F-termination. It will be compared in the etching rate of SiNWs with different doping levels, surface crystalline orientations, and porosity, which can be explained
by the proposed etching mechanism.

7.1 Results and discussion

MACE electrochemically drives nucleated metal (e.g., Ag) particles to anisotropically scratch a Si wafer to produce a random array of nanowires. The direction along which nuclei scratch determines surface crystalline orientations of as-generated nanowires, and the scratching direction can be controlled by etching temperature, concentration of etchants (e.g., HF) and oxidants (e.g., AgNO3, Fe(NO3)3, and H2O2), and crystallographic planes and doping levers of Si wafers. With use of the recipes summarized in Table 1, MACE generates nanowires vertically protruding on wafers with diverse doping levels and crystallographic planes (Figure 7.1a, Figure 7.1d), indicating that surface crystalline orientation of nanowires is in consistence with that of parent wafers (Figure 7.2). MACE of n− and n+-Si creates SiNWs without pores (Figure 7.2a), and that of n12-Si produces mpSiNWs (Figure 7.2b). Since the MACE-generated nanowires duplicate the doping properties and crystalline structures from parent wafers, they are named after their parent wafers, i.e., n−-SiNWs(100) originating from n−-Si(100), n+-SiNWs(100) from n+Si(100), n+-SiNWs(111) from n+-Si(111), n12-mpSiNWs(100) from n12-Si(100), and n12-mpSiNWs(111) from n12-Si(111) (Table 1). It is well-known that HF removes SiO2 and terminates Si with H atoms (i.e., generating H:Si surfaces). The H-termination passivates Si surfaces from further reacting with HF. The HF-induced removal of SiO2 and H-termination are represented in Scheme 7.1a. Fδ− in the polarized Hδ−−Fδ− nucleophilically attacks Siδ−−Oδ− to generate Siδ−−F and Siδ−−OH (Scheme 7.1a, I and II). Since Si−F has higher bond energy than Si−O (5.9 eV vs 4.7 eV), Fδ− of HF is apt to continuously attacking Siδ−−OH to cleave Siδ−−O and create another Siδ−−F (Scheme 7.1a, II and III), resulting in the dissolution of oxides. Si back bonds (Siδ−−Siδ) are polarized and weakened because of the big difference in electronegativity (χ) between F (χF = 3.98) and Si (χSi = 1.9), to
drive HF to cleave the back bonds and graft Siₐ with H (Scheme 7.1a, III and IV). Given $\chi_H$ of 2.1, Si–H has a weak dynamic dipole moment to passivate Si from etching by HF. HF is a weak acid, given by

$$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \quad (7.1)$$

Scheme 7.1 (a) HF-Induced H-Termination on Si, (b) F⁻-Caused Etching of Si, (c) F⁻-Caused Etching of Si(100), and (d) F⁻-Caused Etching of Si(111)\textsuperscript{a}

\textsuperscript{a}“Siₐ” represents a Si atom on surfaces, and it is general to use “Siₐ” and “Siₐ” to denote Si atoms in different layers underneath the surface. The back bonds in (c) and (d) are highlighted in red.

It is HF that dominates the nucleophilic attack. If F⁻ anions dominated the attack, it would result in the complete dissolution of Si. NH₄F hydrolyzes in aqueous solution, given by
\[
\text{NH}_4^+ + F^- + H_2O \rightleftharpoons NH_3 \cdot H_2O^+ + HF \tag{7.2}
\]

40% NH\(_4\)F aqueous solution has pH of \(~8\), in which F\(^-\) anions predominate over HF molecules. Si wafers are also terminated with H in 40% aqueous NH\(_4\)F, indicating that F\(^-\) anions tend to hydrolyze to be HF. The hydrolysis is thermodynamically promoted, since F\(^-\) anions are quite benign and much less reactive than HF. Adachi et al. found that the dissolution of SiO\(_2\) in 1.5% HF is 5.5 times faster than 40% NH\(_4\)F\(^-\).\(^1\)\(^5\)\) The slower dissolution in 40% NH\(_4\)F could be attributed to the contradiction between the predominance of F\(^-\) anions and the nucleophilic attack by HF.

Table 7.1 Summary of semiconductor intrinsic properties of Si wafers, conditions of MACE, NH\(_4\)F-etching rate, and atomic percentage ratio of F\(_{1s}\)% to Si\(_{2p}\)%.

<table>
<thead>
<tr>
<th>Si Wafers</th>
<th>Dopant</th>
<th>Electrical resistivity ((\Omega)-cm)</th>
<th>MACE</th>
<th>NH(_4)F-etching rate (nm/min)</th>
<th>F(<em>{1s}) / Si(</em>{2p})</th>
<th>(x) in Si-F_x</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n^+)-Si(100)</td>
<td>P</td>
<td>1-10</td>
<td>2.4</td>
<td>0.02</td>
<td>NC</td>
<td>35</td>
</tr>
<tr>
<td>(n^-)-Si(100)</td>
<td>Sb</td>
<td>0.008-0.02</td>
<td>2.4</td>
<td>0.02</td>
<td>NC</td>
<td>35</td>
</tr>
<tr>
<td>(n^-)-Si(111)</td>
<td>Sb</td>
<td>0.01-0.018</td>
<td>4.8</td>
<td>0.02</td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>(n^+)-Si(100)</td>
<td>As</td>
<td>0.001-0.005</td>
<td>4.8</td>
<td>0.02</td>
<td>NC</td>
<td>35</td>
</tr>
<tr>
<td>(n^+)-Si(111)</td>
<td>As</td>
<td>0.001-0.005</td>
<td>4.8</td>
<td>0.02</td>
<td>NC</td>
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</tr>
</tbody>
</table>

After the immersion in 40% aqueous NH\(_4\)F, it is general to find out that nanowires significantly shorten and surface density of nanowires in the arrays reduces with immersion duration (Figure 7.1), illustrating that NH\(_4\)F etches nanowires without surface passivation. It was known that F\(^-\) anions can etch Si; hence, it is proposed in Scheme 1b that F\(^-\) anions dominate the nucleophilic attack over HF. With assistance of NH\(_4^+\) cations, F\(^-\) anions dissolve SiO\(_2\) with byproducts of NH\(_3\) and...
H$_2$O (Scheme 1b, I–III). The generation of NH$_3$ accounts for the bubbling during the immersion of samples in 40% aqueous NH$_4$F. After the dissolution of native oxides, Si surfaces are F-terminated (Scheme 7.1b, III). Without the H-termination by HF, F$^-$ anions continuously etch Si (Scheme 7.1b, III–V). It is ambiguous in 40% aqueous NH$_4$F why HF molecules dominate the nucleophilic attack to the surfaces of bulky Si, but F$^-$ anions predominate to one-dimensional nanowires.

**Figure 7.1** Etching of n$^+$-SiNWs(100) by 40% NH$_4$F with duration of (a) 0 min, (b) 3 min, and (c) 5 min; and that of n$^+$-mpSiNWs(100) with duration of (d) 0 min, (e) 0.5 min, and (f) 1 min. (a–f) SEM cross sectional images. The scale bars represent 1 μm.

The proposed mechanism in Scheme 1b was confirmed by diverse spectral characterization. The stretching mode of Si–H$_x$ (i.e., $\nu$(Si–H$_x$)) is located at $\sim$2080 cm$^{-1}$.$^{153}$ $\nu$(Si–H$_x$) was not detected by ATR-FTIR on all NH$_4$F-treated samples (as highlighted by the gray bands in Figure 7.3), illustrating no H-termination. $\nu$(Si–F) is located at $\sim$840 cm$^{-1}$, which was only detected on the NH$_4$F-treated n$^{+2}$-mpSiNWs(111) (as highlighted by the blue band in Figure 7.3b). But XPS detected F$_{1s}$ on all NH$_4$F-etched samples (Figure 7.4), strongly justifying the F-termination induced by F$^-$ anions. All samples have F$_{1s}$ at $\sim$687.3 eV assigned to Si–F$_x$ with $x$ of $\sim$2, and only n$^+$- SiNWs(111) have an additional peak at 689.9 eV attributed to Si–F$_x$ with $x$ of $\sim$3.$^{160}$ It is illustrated that the F-termination on n$^+$-SiNWs(111) has
x in the range of 2–3, and the rest has x of ~2 (Table 7.1). On Si(100), each Siₐ atom connects to two Siₐ atoms via two back bonds (Scheme 7.1c). Each back bond will be attacked by one F⁻ anion so that each Sia will be terminated with two F atoms accounting for x of ~2 on n⁻-SiNWs(100) and n⁻-SiNWs(100). As a comparison, on Si(111) each Sia atom has three back bonds (Scheme 7.1d), resulting in the termination of Siₐ with three F atoms. The etching along [100] is thermodynamically preferential, since the etching needs to cleave two back bonds along [100] but three along [111]. Therefore, n⁺-SiNWs(111) are etched along not only [111] but also [100], leading to x of 2–3. Although mpSiNWs grow along a certain crystalline direction during MACE, the porosified surfaces of Si skeletons appear to have random crystalline planes. The thermodynamic preference of etching along [100] renders x of ~2 on both n⁻²-mpSiNWs(100) and n⁺²-mpSiNWs(111).

![Figure 7.2 TEM images: (a) n⁻-SiNWs(100); (b) n⁺²-mpSiNWs(100).](image)

The F-termination was further confirmed by PL spectroscopy. The as-generated n⁺²-mpSiNWs(100) with native oxides have a broad reddish PL peak centered at ~680 nm (Figure 7.5a), consistent with the previous reports. The reddish peak is attributed to surface states at the oxide/Si interfaces induced by the porosification. n⁺²-mpSiNWs(100) were terminated with H in 5% HF, leading to a slight red shift of the reddish peak to ~710 nm. As comparison, the treatment of 40% NH₄F barely shifts the reddish peak and creates a broad blue peak centered at ~420 nm. It was reported that plasma enhanced chemical vapor deposition in the
mixtures of SiF$_4$–SiH$_4$–H$_2$ was employed to generate nanocrystalline Si films (nc-Si) terminated with H and F.\textsuperscript{162} The nc-Si has two broad PL peaks centered at $\sim$710 and $\sim$540 nm, ascribed to Si–H and Si–F, respectively.\textsuperscript{163} It is consistent in Figure 7.6a to detect PL at $\sim$710 nm induced by the H-termination, and it is deduced that the blue peak centered at $\sim$420 nm stems from the F-termination. The difference in the blue peak position of n$^{+2}$-mpSiNWs(100) from nc-Si can be attributed to two factors. The first is the stoichiometric parameter x in Si–Fx. n$^{+2}$-mpSiNWs(100) has x of $\sim$2, but it was unknown on nc-Si. The second is the surface topography. Compared to relatively smooth surfaces of nc-Si, n$^{+2}$-mpSiNWs(100) have porous surfaces with numerous defects. The two factors will sensitively shift the PL peak.

The pristine n$^{-}$-SiNWs(100) emit a weak reddish PL at $\sim$650 nm (Figure 7.5b). Although without porosified surfaces, n$^{-}$-SiNWs(100) appear to have rough surfaces (Figure 7.2a) that may have special surface states at the oxide/Si interfaces, accounting for the reddish PL analogous to n$^{+2}$-mpSiNWs(100). With a lack of surface porosification, n$^{-}$-SiNWs(100) have much less amount of surface states to emit weak reddish PL. The F-termination creates a broad PL peak centered at $\sim$490 nm (Figure 7.5b). Both n$^{-}$-SiNWs(100) and n$^{+2}$-mpSiNWs(100) have x of $\sim$2 so that the difference in the blue peak position may originate from the surface topography, i.e., rough versus porosified surfaces.

The NH$_4$F etching rate can be quantitatively evaluated in terms of the reduction in length or surface density. The NW length can be readily measured from cross-sectional SEM images, e.g., Figure 7.1. Although the surface density could be evaluated from top-down SEM images, the bad contrast of nanowires to the underneath Si wafer from the top-down view makes it hardly to accurately measure the surface density. Herein, the etching rate is evaluated with respect to the NW length.
Figure 7.6 summarizes the etching-caused shrinkage in NW length, and a few points should be brought to attention. First, n$^{+2}$-mpSiNWs with (100) and (111) continuously shorten with etching, but the three kinds of SiNWs are intact in the first 1 min, followed by the continuous shrinkage in length. The as-generated SiNWs and mpSiNWs spontaneously oxidize in ambient conditions, and it was detected by ATR-FTIR the first-order transverse optical (TO) phonon stretching of SiO$_x$ at $\sim$1050 cm$^{-1}$ indicating x of 1.5 (Figure 7.3).$^{164}$ NH$_4$F eliminates the TO mode in Figure 7.4a, illustrating the removal of SiO$_x$ on SiNWs. It is indicated that NH$_4$F removes SiO$_x$ and then commences to etch SiNWs, accounting for the resistance of SiNWs to the initial NH$_4$F etching. On the contrary, the TO mode of SiO$_x$ was still detectable on the NH$_4$F-etched mpSiNWs (Figure 7.4b). The continuous shortening of mpSiNWs and the coexistence of SiO$_x$ illuminate that NH$_4$F simultaneously removes SiO$_x$ and porosified Si skeletons. There are a large amount of structural defects on the porosified surfaces of mpSiNWs (Figure 7.3b). NH$_4$F would preferentially etch Si skeletons at the surface defects that are not effectively passivated by the oxide layers. Solid SiNWs appear to have relatively smooth surfaces with much less amount of surface defects (Figure 7.2a) so that the removal of Si should take place after the dissolution of the passivation oxide layer. Second, analogous to n$^{+2}$-mpSiNWs, the three kinds of SiNWs shrink in length linearly with etching duration after the complete removal of SiO$_x$. The slope of the linear evolution was fit in Figure 7.6, equal to the etching rate. The etching rate of diverse nanowires is summarized in Table 1 in the order of n$^{-}$-SiNWs(100) < n$^{+}$-SiNWs(100) < n$^{+2}$-mpSiNWs(100) < n$^{+2}$-mpSiNWs(111) < n$^{-}$-SiNWs(111). Third, note that the NH$_4$F etching is along three-dimensional in the nanowire arrays so that the etching should be fully studied in the longitudinal direction using the length-related etching rate and in the horizontal two-dimension using surface density-related etching rate. Other techniques should be employed to accurately evaluate the etching evolution of surface density.
Figure 7.3 ATR-FTIR spectra of (a) SiNWs and (b) mpSiNWs before and after 40% NH₄F etching. The etching duration is shown in the plots. The light pink bands highlight the first TO mode of SiOₓ. The gray bands illustrate no detection of $\nu$(Si–Hₓ), and the blue band highlights that $\nu$(Si–F) was only detected on the NH₄F-treated n⁺²-mpSiNWs(111). “$\nu$” denotes the stretching mode.

Figure 7.4 XPS spectra of F₁s of diverse SiNWs etched by 40% NH₄F in 2 min (for n⁻-(100), n⁺⁻(100), and n⁺⁻(111)) and 0.5 min (for n⁺²-(100) and n⁺²-(111)). “CPS” represents the intensity in counts per second.

There are three factors determining the etching rate. The first factor is the doping level. Dopant atoms substantially disturb the back bonds so that high doping level will facilitate the nucleophilic attack to back bonds and etching of Si. The second factor is atomic percentage ratio of F₁s to Si₂p (i.e., F₁s/Si₂p), which was measured
by XPS and summarized in Table 1. Under high ratio, more back bonds are weakened by the F-termination to promote the NH₄F etching. The ratio F₁s/Si₂p is compared in two groups: one is the three kinds of SiNWs etched in 40% NH₄F for 2 min, and another is the two kinds of mpSiNWs etching for 0.5 min (as highlighted by two light pink bands in Figure 7.6). The reason not to etch all the samples in 2 min is that mpSiNWs are etched in 40% NH₄F too quickly to survive after 2 min. It is illustrated in each group that the higher is F₁s/Si₂p, the faster is the etching. The 0.5 min etching makes n⁺²-mpSiNWs(111) have F₁s/Si₂p of 0.0269, the highest compared to the 0.5 min etched n⁺²-mpSiNWs(100) and the three kinds of SiNWs etched for a longer duration of 2 min. It accounts for that ν(Si−F) can be only detected on the etched n⁺²-mpSiNWs(111) (Figure 7.4). The rest may have the intensity of ν(Si−F) below the detection limit of ATR-FTIR. The third factor is the stoichiometric x of Si−Fx. The back bonds become more vulnerable with increasing value of x. Note that the ratio F₁s/Si₂p should be decoupled with the value x. The stoichiometric x represents the number of F atoms attaching to one Si atom during the NH₄F etching, and the ratio F₁s/Si₂p evaluates the total number of F atoms terminated on nanowires. The decoupling originates from that not all Si atoms can be nucleophilically attacked on the MACE-generated rough surfaces, especially on the porosified surfaces of mpSiNWs. The order of the etching rate can be explained by the three factors. The etching rate of NWs(100) increases with the doping level (n⁻-SiNWs(100) < n⁺-SiNWs(100) < n⁺²-mpSiNWs(100)), attributed to the first factor. On the contrary, the etching of n⁺-SiNWs(111) is slightly faster than that of n⁺²-mpSiNWs(111), owing to the trade-off between the first and third factor. The first factor will cause the etching of n⁺-SiNWs(111) to be slower than that of n⁺²-mpSiNWs(111), but the third factor gives rise to the opposite result. The third factor overbalances the second, accounting for the slightly faster etching of n⁺-SiNWs(111) than n⁺²-mpSiNWs(111). At last, the etching on NWs(100) is slower than NWs(111) with respect to the same doping level. The etching is faster on n⁺-SiNWs(111) than
n⁺-SiNWs(100), ascribed to the second and third factor. Only the second factor accounts for the slower etching of n⁺²-mpSiNWs(100) than n⁺²-mpSiNWs(111).

Figure 7.5 PL spectra: (a) n⁺²-mpSiNWs(100) etched by 40% NH₄F for 1 min and 5% HF for 5 min; (b) n⁻-SiNWs(100) etched by 40% NH₄F for 2 min. The system noise in the homemade PL setup gives rise to the peaks marked by asterisks.

Figure 7.6 NH₄F-etching evolution of diverse SiNWs in terms of NW lengths. Solid lines fit the linear etching evolution to evaluate the NH₄F-etching rate. Dash lines illustrate that there is no apparent change within the first 1 min for three kinds of SiNWs (i.e., n⁻-(100), n⁺-(100), and n⁺-(111)). XPS is operated to evaluate the ratio of F₁s % to Si₂p %, and the comparison is made among the 2 min etched SiNWs (n⁻-(100), n⁺-(100), and n⁺-(111)) and between 0.5 min etched mpSiNWs (n⁺²-(100) and n⁺²-(111)), which are highlighted by two light pink bands.
### 7.2 Conclusion

Si nanowire arrays are intact in HF because of H-passivation but etched in 40% aqueous NH$_4$F with pH of ~8 in which F$^-$ and NH$_4^+$ ions are dominant. The NH$_4$F etching is attributed to F$^-$ anions nucleophilically attacking Si atoms to terminate Si with F atoms. The grafted Si–F bonds have strong dipole moment to significantly polarize and weaken Si back bonds.

The polarized back bonds are vulnerable to the nucleophilic attack of F$^-$ anions, resulting in the dissolution of nanowires. The F-termination is confirmed by ATR-FTIR, XPS and PL spectroscopy. Chen$^{155}$ et al. ascribed the NH$_4$F etching to the OH termination, since it is at pH of ~8 that the H-termination is unstable and tends to hydrolyze to be the OH termination. As comparison, we propose that the OH termination is only a part in the removal of oxides (Scheme 7.1b, I and II). The OH termination will be further attacked by F$^-$ anions, leading to the etching of nanowires (Scheme 7.1b, II–V). The etching rate in terms of the NW length is evaluated in the order of n$^-$-SiNWs(100) < n$^+$-SiNWs(100) < n$^{+2}$-mpSiNWs(100) < n$^{+2}$-mpSiNWs(111) < n$^+$-SiNWs(111), which could be explained by three factors including the doping level, atomic ratio F$_{1s}$/Si$_{2p}$, and the stoichiometric x of the surface termination Si–Fx. An increase in doping levels leads to acceleration of the etching of NWs(100) but slight slowing of the etching of NWs(111). Given that the etching is promoted by the F-termination induced polariztion of Si back bonds, the stoichiometric x of n$^{+2}$-mpSiNWs(111) is smaller than that of n$^+$-SiNWs(111), accounting for the unexpected slowing. At the same doping level, NWs(100) are etched more slowly than NWs(111), attributed to the smaller ratio F$_{1s}$/Si$_{2p}$ of NWs(100) than NWs(111). The smaller value of x on the etched n$^+$-SiNWs(100) than n$^+$-SiNWs(111) further accounts for the slower etching of n$^+$-SiNWs(100) than n$^+$-SiNWs(111). At the initial etching stage, 40% NH$_4$F removes surface oxides and then commences to etch solid SiNWs. However, the removal of surface oxides and
Si skeletons simultaneously occurs on mpSiNWs, since native oxides cannot fully
passivate the porosified surfaces of mpSiNWs compared to the relatively smooth
surfaces of solid SiNWs. This work contributes to understanding the difference in
surface reactions between bulky Si and one-dimensional SiNWs, quantitatively
analyzing the NH₄F-caused etching of SiNWs and providing useful information
about surface processing and modification of SiNW-based nanoelectronic devices.
This work has been published in *J. Phys. Chem. C* (2014, *118* (31), 17870).¹⁶⁵
Chapter 8 Engineering of photoluminescence of mesoporous silicon nanowires through molecular grafting

mp-SiNWs can be created by metal-assisted chemical etching (MACE)\textsuperscript{87, 89}, electrochemical etching\textsuperscript{103} and electrochemical laser-induced etching. Molecules graft on Si surfaces in two ways. The silanization of SiO\textsubscript{2}-covered Si immobilizes molecules via Si-O-C bonds, and the hydrosilylation of H:Si creates Si-C contacts. The grafting via Si-C is preferential over Si-O-C contacts, since the Si-C contacts give rise to smooth monolayer topography\textsuperscript{166}, high chemical stability\textsuperscript{167-168}, small interfacial trap densities\textsuperscript{169}, and high electric conductivity\textsuperscript{170-171}. Herein, mp-SiNWs will be generated by MACE, and thermal hydrosilylation will be operated to modify mp-SiNWs via Si-C contacts. 1,4-diethynylbenzene (DEBZ) will be mono-silylated on mp-SiNWs to retain the conjugation configuration (Scheme 8.1a).

\textbf{Scheme 8.1} (a) Thermal mono- and bis-silylation of DEBZ on a H:Si surface. (b) Mono-silylated SiNWs on a Si wafer.
The conjugation monolayer is desired ascribing to two reasons. First, the benzene-involved conjugation systems are apt to creating face-to-face, close-packed configuration, favorable for high chemical stability and surface passivation against ambient oxidation. Second, the conjugated π-structures can magnify the electrical response to external disturbance, leading to high detection sensitivity required for bio-sensors, security checking, air quality control and environmental pollution monitoring. The mono-silylation will be operated at modest temperature, and evaluated by ATR-FTIR (attenuated total reflectance-Fourier transform infrared spectroscopy) and photoluminescence (PL). The grafting will be optimized with hydrosilylation duration, in terms of surface coverage and antioxidation effect quantitatively evaluated by XPS (X-ray photoelectron spectroscopy). The mild mono-silylation will be operated on solid SiNWs with surface crystallographic plane of (100) and (111), and the optimized grafting will be compared between mp-SiNWs and SiNWs in terms of surface coverage and passivation against ambient oxidation. The experimental conditions of MACE are summarized in Table 8.1.

8.1 Results and Discussion

Scheme 8.1a illustrates the mono-silylation of DEBZ on H:Si. DEBZ attaches to Si via one of two terminating -C≡CH groups to form a Si-C bond per molecule, accompanied with the reduction of -C≡CH to C=C for creating a Si-C=C contact. The mono-silylated C=C bond may be further reduced to C-C under appropriate conditions, leading to the grafting via two Si-C bonds per molecule (i.e. bis-silylation, in the 1,1- and 1,2-bridged configurations) \(^{172}\). The 1,1-bridged configuration is energetically favorable, but the 1,2-bridged may be formed at temperature over 200 °C \(^{173}\). The bis-silylation introduces an uncertainty in the contact configuration, not desired in e.g. molecular electronics since charge transport sensitively depends on the contact structures \(^{174}-^{175}\). Chidsey et al. claimed
that without sufficient thermal excitation, the modest hydrosilylation at 100 °C could effectively prohibit the bissilylation of alkyne on Si(111)\(^{167}\). Therefore, it is tentative to immobilize DEBZ on mp-SiNWs at modest temperature of 110 °C, far below the melting point of the solvent mesitylene (164.7 °C).

Table 8.1 The experimental conditions of MACE. “RT” represents room temperature.

<table>
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<tr>
<th>Wafers</th>
<th>[HF] (mol/L)</th>
<th>[AgNO(_3)] (mol/L)</th>
<th>(T) (°C)</th>
<th>t (min)</th>
<th>Stirring</th>
<th>Products</th>
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<td>mp-SiNWs</td>
</tr>
<tr>
<td>(n^+)-Si(100)</td>
<td>2.4</td>
<td>0.02</td>
<td>RT</td>
<td>20-30</td>
<td>x</td>
<td>SiNWs(100)</td>
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<td>70</td>
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</table>

Figure 8.1 Mild mono-silylation of mp-SiNWs(100) with DEBZ for 20 hr. SEM cross-sectional images: (a) the pristine and (b) DEBZ-grafted mp-SiNWs, in the bottom portions of mp-SiNW arrays. The circle inset in (a) is a TEM image of a mp-SiNW, and the rectangle insets in (a) and (b) magnify the roots of mp-SiNWs.

![Figure 8.1](image-url)
**Figure 8.2** ATR-FTIR spectra: (a) the pristine mp-SiNWs (in black, R% is magnified by 2 times) and H:mp-SiNWs (in red); (b) mp-SiNWs mono-silylated for 6 hr (in black), 12 hr (in red) and 20 hr (in green). Diverse vibration modes of benzene in DEBZ are marked by asterisks. “ν” denotes the stretching mode.

**Figure 8.3** XPS spectra of mp-SiNWs(100) mono-silylated for 6 hr (in black), 12 hr (in red) and 20 hr (in green): (a) C1s and (b) Si2p. “CPS” represents the unit of counts per second. (c) A plot of ϑ_{DEBZ} as function of mono-silylation duration. (d) A plot of Si2p-O% under the mono-silylation lasting 6, 12 and 20 hr: the as-grafted (solid red dots) and 2-month-ageing samples (hollow red dots). The solid black triangles represent the ageing-induced increase in Si2p-O%.

### 8.1.1 Thermal mono-silylation of mp-SiNWs

MACE of n^{+2}-Si(100) creates close-packed mp-SiNWs in a length of ~1.5 μm, vertically protruding on a layer of mesoporous Si (mpSi, Figure 8.1a). After 20-hr mild hydrosilylation at 110 °C, the surfaces of mp-SiNWs appear to be rough (Figure 8.1b versus 11a), indicating the immobilization of DEBZ. ATR-FTIR
(Figure 8.2a) illustrates that the pristine mp-SiNWs have a dominant vibration peak at 1062 cm\(^{-1}\), assigned to the transverse optical (TO)-phonon stretching mode of SiO\(_x\) (i.e. \(\nu(\text{SiO}_x), x: 1.5\sim2\)).\(^{153,164}\) The HF treatment eliminates the TO mode, and generates two peaks at 904 and 2091 cm\(^{-1}\). The first is assigned to the umbrella model of SiH\(_3\) or the scissor mode of SiH\(_2\), and the second is \(\nu(\text{SiH}_3)\)^{155}. It is illustrated that HF completely remove SiO\(_x\) and passivate mp-SiNWs with hydrogen, i.e. H:mp-SiNWs. Scheme 2a shows that the mono-silylation of DEBZ creates a “Si-C=C” contact; the benzene ring and one of two terminating groups of -C≡CH are intact. After 20-hr mild hydrosilylation, it was detected by ATR-FTIR in Figure 8.2b \(\nu(\text{C≡C})\) at ~2090 cm\(^{-1}\), \(\nu(\text{Si-C=C})\) at ~1600 cm\(^{-1}\)^{176}, and a set of benzene involved vibrations in 1500-900 cm\(^{-1}\) (marked by asterisks, match well with the corresponding vibrations in the FTIR spectrum of DEBZ powders. It is from the molecular level to demonstrate the mono-silylation of DEBZ on mp-SiNWs at 110 °C. The inset in Figure 8.1b clearly shows that the mild mono-silylation can effectively immobilize DEBZ at the roots of mp-SiNW arrays, illustrating that 110 °C is high enough to promote the silylation solution sufficiently diffusing into the close-packed arrays, and mp-SiNWs are throughout modified along the longitudinal axes. Note that ATR-FTIR has an effective path length of 1.48-0.19 μm in the wavenumber range of 500-4000 cm\(^{-1}\). The asgenerated mp-SiNWs are longer than the effective IR path length, so that ATR-FTIR could barely detect DEBZ binding to the underneath mpSi and/or bulky Si. While the mono-silylation lasts shorter than 12 hr, it could be detected \(\nu(\text{C≡C})\) and the set of benzene-involved vibrations (Figure 8.2b). However, \(\nu(\text{Si-C=C})\) turns to be a shoulder peak after the 6-hr mono-silylation, and the 12-hr grafting makes \(\nu(\text{Si-C=C})\) significantly shift to ~1650 cm\(^{-1}\). Either low vibrational intensity or peak shift of \(\nu(\text{Si-C=C})\) may stem from the formation of non-compact monolayers, leading to the deterioration of surface passivation against Si oxidation. The grafting can be quantitatively evaluated by surface coverage \(\theta_\text{DEBZ}\) via XPS. X-rays in XPS have a
penetration length of ~1 μm, and the escape depth of ejected electrons is ~10 nm underneath the grafted surfaces. Since mp-SiNWs are longer than the X-ray penetration length, XPS evaluates $\theta_{\text{DEBZ}}$ of the upper portion of mp-SiNW arrays, as represented by the red dashed box in Scheme 8.1b. By measuring $C_{1s}$% (Figure 8.3a) and $Si_{2p}$% (Figure 8.3b), $\theta_{\text{DEBZ}}$ was calculated, which can be larger than 1 according to the formula. $\theta_{\text{DEBZ}}$ of mp-SiNWs increases with monosilylation duration, from 1.44 at 6 hr to 1.62 at 12 hr, and 1.80 at 20 hr (Figure 8.3c). Si$_{2p}$-O atomic percentage ($Si_{2p}$-O%) of the as-grafted and ageing mp-SiNWs are summarized in Figure 8.3d. After 6-hr mono-silylation, the freshly-modified mp-SiNWs have 2.5% Si$_{2p}$-O (at ~104 eV, Figure 8.3b). The elongation of mono-silylation beyond 12 hr significantly diminishes Si$_{2p}$-O% below the XPS detection limit. The 2-month ageing causes Si$_{2p}$-O% increase in 5.17% on the 6-hr mono-silylated mp-SiNWs, 4.68% on the 12-hr, and only 2.94% on the 20-hr (the solid black triangles in Figure 8.3d). It is consistent that the higher surface coverage of DEBZ, the better anti-oxidation. Hence, the mono-silylation of mp-SiNWs is optimized under 20-hr grafting.

**8.1.2 Thermal mono-silylation of SiNWs without pore**

The mild mono-silylation of DEBZ can be adapted to modifying solid SiNWs. Analogous to mp-SiNWs, the modest grafting apparently roughens SiNWs(100) throughout along the longitudinal axes. The grafting-induced roughening was also observed on SiNWs(111), which isn’t shown here. It has been detected by ATR-FTIR the three sets of characteristic vibration modes, demonstrating the mono-silylation with DEBZ on both SiNWs(100) and SiNWs(111). Evaluated by XPS, $\theta_{\text{DEBZ}}$ of SiNWs(100) has a maximum of 2.53 after 12-hr mono-silylation, compared to 1.99 at 6 hr and 2.30 at 20 hr (Figure 8.4a). Si$_{2p}$-O% is not detectable after 12-hr mono-silylation, but is 1.96% at 6 hr and 0.99% at 20 hr (the red solid dots, Figure 8.4b), consistently illustrating that the optimization of $\theta_{\text{DEBZ}}$ results in
the most effective passivation of SiNWs against oxidation. The 5-month ageing
effectively oxidizes the DEBZ-grafted SiNWs(100), and the ageing induced
increase in Si\textsubscript{2p}-O\% declines from 1.47\% at 6 hr to 1.08\% at 12 hr and only 0.10\%
for 20 hr (the solid black triangles, Figure 8.4b).

**Figure 8.4** A plot of $\theta_{\text{DEBZ}}$ of (a) SiNWs(100) and (c) SiNWs(111), as function of mono-
silylation duration (6, 12 and 20 hr). A plot of Si\textsubscript{2p}-O\% of the as-grafted and ageing samples:
(b) SiNWs(100), 5-month ageing; (d) SiNWs(111), 2-month ageing.

Compared to the 12-hr mono-silylation, the 20-hr grafting tends to more effectively
prevents the ageing of SiNWs(100), but have less $\theta_{\text{DEBZ}}$ and weaker vibration
intensity of $\nu$(Si-C=C). As a result, it is compromised that the mono-silylation of
SiNWs(100) is optimized under 12-hr grafting. Furthermore, the mono-silylation
of SiNWs(111) is optimized at 20 hr, due to the maximum $\theta_{\text{DEBZ}}$ of 2.12 (Figure
8.4c) and minimum ageing induced increase in Si\textsubscript{2p}-O\% of 0.40\% (Figure 8.4d).
The covalent grafting of DEBZ can be further confirmed by PL. The pristine mp-
SiNWs have a broad reddish PL peak centered at $\sim$675 nm (Figure 8.5a), attributed
to the porosified surface states. SiNWs(100) and SiNWs(111) barely have detectable PL in a wavelength range of 350-850 nm (Figure 8.5b-c). The optimized grafting of DEBZ gives rise to a broad PL peak centered at ~510 nm on the three kinds of NW arrays, having an apparent blueshift from the PL peak of non-grafted DEBZ centered at ~560 nm (Figure 8.5a-c). The blueshift may be mainly attributed to the orbital hybridization of DEBZ to Si via the formation of Si-C=C contacts and/or the reduction of one of two C≡C terminal groups. It is demonstrated that surface modification can transfer PL of grafted molecules to SiNWs with some grafting induced spectral shift, opening a door to flexibly engineer the optical properties of SiNWs with diverse porosities for optoelectronic and bio-detection applications.

**Figure 8.5** PL spectra of DEBZ powders (in green, the PL intensity is reduced by 100 times), pristine NWs (in black, the PL intensity is magnified by 20 times), optimized DEBZ-grafted NWs: (a) mp-SiNWs(100), (b) SiNWs(100), (c) SiNWs(111).

**Table 8.2** Summary of $\theta_{DEBZ}$, the normalized $\theta_{DEBZ}$ and anti-ageing of diverse optimized DEBZ-grafted SiNWs. $D_{sdd}(100)=6.78\times10^{14}$ cm$^{-2}$, and $D_{sdd}(111)=7.83\times10^{14}$ cm$^{-2}$.

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<th>Samples</th>
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8.1.3 Comparison of the optimized mono-silylation among diverse NW arrays

Table 8.2 summarizes the comparison in the optimized mono-silylation on diverse NW arrays, in terms of surface coverage and ageing-enhanced Si$_{2p}$-O%. $\theta_{\text{DEBZ}}$ of mp-SiNWs and SiNWs(100) is normalized by $D_{\text{Si(100)}}$, and that of SiNWs(111) is normalized by $D_{\text{Si(111)}}$. The normalized $\theta_{\text{DEBZ}}$ is in an order of SiNWs(100) > SiNWs(111) > mp-SiNWs. Note that the normalization is suitable for smooth surfaces of SiNWs, and is overestimated for the porosified surfaces of mp-SiNWs. But the overestimation on mp-SiNWs doesn’t change the order of the normalized $\theta_{\text{DEBZ}}$. The optimized mono-silylation can effectively passivate the freshly-grafted surfaces, so that Si$_{2p}$-O% is all below the detection limit on the three kinds of SiNWs. The surface passivation is deteriorated with low surface coverage, so that the mono-silylated mp-SiNWs are the most vulnerable to the ambient ageing, clearly illuminated by the ageing-induced increase of Si$_{2p}$-O%. It is attributed to that SiNWs have relatively smooth surfaces, but the porosification in mp-SiNWs causes so large amount of surface defects (the circle inset in Figure 8.1a)\textsuperscript{113} that the monosilylation can hardly passivate them all.

8.1.4 The mono-silylation mechanism

Silicon hydrosilylation with alkene or alkyne can be initiated by the homolytic cleavage of a Si-H dangling bond to create a silyl radical, followed by a chain reaction between silyl radicals and unsaturated C-C bonds\textsuperscript{177}. Si-H bonds have bond energy in the range of 80-90 kcal/mol\textsuperscript{178}. Thermal hydrosilylation typically operates below 200 °C\textsuperscript{26,42}, under which it is not clear how the homolytic cleavage could occur at an appreciable rate. However, trace molecular oxygen in the deoxygenated solution can abstract hydrogen to create silyl radicals\textsuperscript{179}. The activation energy of this process was evaluated as ~30 kcal/mol\textsuperscript{180}, indicating that
the trace oxygen-induced generation of silyl radicals can occur in the moderate mono-silylation at 110 °C \(^{180}\). Alternatively, four non-radical mechanisms may account for the mild monosilylation. First, the fluoride-catalyzed stepwise mechanism\(^{181}\). The H-termination induced by HF leaves F- to attack interfacial Si atoms, resulting in pentavalent Si intermediate ions that transfers a hydride to the -C≡CH terminal group to generate -CH=HC- carbanions. The carbanions attack the F-polarized Si centers to release F-, leading to the molecular grafting via the Si-C=C contacts. Second, a direct concerted mechanism involves a four-atom transition state between -C≡CH and Si-H dangling bonds.\(^{178}\) The concerted pathway has an energy barrier in the range of 56-66 kcal/mol, lower than that of the homolytic cleavage of a Si-H bond; hence, it may be favorable for the mild monosilylation to follow the concerted pathway. Third, the Zwitterion-based mechanism\(^{178,181}\). The electron-rich -C≡CH terminal attacks a surface Si atom to form a Zwitterionic pentavalent Si intermediate ion, and then a hydride transfers from the polarized Si center to β-C of the terminal. The Zwitterionic pathway is thermodynamically indistinguishable from the concerted pathway. Fourth, the degradation of hydrocarbons catalyzed by the silanol groups on the surface of glass vessels may initiate the mild mono-silylation \(^{182}\). More studies should be carried out to disclose the mechanism of the mild mono-silylation of DEBZ on SiNWs with smooth and porosified surfaces.

**8.2 Conclusions**

In deoxygenated mesitylene containing 0.2 mol/L DEBZ, mp-SiNWs are mono-silylated with DEBZ at modest temperature of 110 °C. The mono-silylation creates Si-C=C contacts to immobilize DEBZ, and retains the molecular conjugation configuration. The covalent grafting accompanied with a change of the molecular structure of DEBZ renders the PL of DEBZ have an apparent blueshift. The modest monosilylation is generally adapted to SiNWs(100) and SiNWs(111). By
quantitatively evaluating surface coverage and anti-oxidation, the mono-silylation is optimized with reaction duration of 20 hr for mp-SiNWs and SiNWs(111), and 12 hr for SiNWs(100). The optimized mono-silylation generates the most compact monolayers on SiNWs(100), followed by SiNWs(111) and mp-SiNWs(100). Compared to relatively smooth surfaces of SiNWs, mp-SiNWs appear to have porosified surfaces with numerous surface defects that could not be effectively passivated by the grafted monolayers. As a result, the DEBZ-grafted mp-SiNWs have the smallest surface coverage and are the most vulnerable to the ambient oxidation. The mono-silylated DEBZ monolayers retain unsaturated $\text{C}≡\text{C}$ bonds at the free ends, which have high chemical activity. Therefore, this work comes up with a modest thermal method to modify mp-SiNWs with chemically active monolayers facilely subjected to further surface modification. It should be emphasized that it is of critical importance to passivate surface defects of mp-SiNWs if device functions would be deteriorated by ambient oxidation, which is under study recently.
Chapter 9 Conclusions and Perspective

9.1 Conclusions

In this dissertation, I present my study of the optical properties of two kinds of emerging nanostructure: plasmonic helical NPs and mesoporous SiNWs.

I found a method that neglects the helix geometrical limit of \( P > d \) and performed GLAD under fast substrate rotation to generate AgNPs that have hidden helicity with nominal \( P < d \). These chiral AgNPs arrays with a nominal \( P \) in the range of 3 to 70 nm have chiroptical activity in the UV–visible region. The LSPR barely shifts, but the CD intensity tends to see a common logarithmic increase with nominal \( P \).

The deposition is performed with a regular \( T_{\text{sub}} \) to avoid the integration of GLAD with an extremely low-\( T_{\text{sub}} \) 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 chiral plasmonics that approach physical limits and exploit significant chirality-related bio-applications to tackle important health and environmental problems.

I then applied this GLAD-related fast substrate rotation approach to generate chiral Al nanostructures with chiroptical response in the UV–visible region. I used another method to fabricate Al nanostructures with chiroptical response that deposits Al onto the host of chiral plasmonic NPs, such that the structural helicity is duplicated from the chiral host to the achiral guest of Al nanocappings. I demonstrated a new method of chirality transfer from chiral host to achiral guest that can induce achiral guests made of some plasmonic materials that are not facilely sculpted in the helical to synergistically producing nanoplasmons with tailorable, broadband, strong chiroptical activity in the UV–visible–NIR region.

Because the manipulation of the CPL to catalyze asymmetric syntheses has fundamental and practical significance, I used plasmonic nanohelices as the substrate for photochirogenic dimerization of AC. As the chirally helical surface-
induced enantioselective adsorption of AC dimers, this asymmetric dimer adsorption gives rise to the enantioselective photocyclodimerization. In contrast, the NHs work to amplify the near-field optical chirality on the surface of the nanohelices, and the helical handedness determines the enantioselectivity of the products: the left/right handedness of the AgNHs gives rise to the ee value with a positive/negative sign. Therefore, this AgNH-mediated enantioselective photocyclodimerization can be ascribed to the synergistic contribution from the chirally helical surface-induced enantioselective adsorption of the anti-IIH dimers and the chiroptically active nanoplasmon-enhanced optical chirality of CPL.

In contrast, MACE is performed to generate mesoporous SiNWs (mp-SiNWs) with mesopores from 2 to 50 nm. Because of the importance of engineering the porosity of SiNWs, I devised a new method to reduce the porosity of mp-SiNWs with no change in the MACE conditions. After generating the mp-SiNWs with high porosity, the mp-SiNWs are removed from the mother Si wafers with sticky tape, leaving a chemically active mesoporous residue exposed to the second MACE. Thicker Ag dendrites were generated during the second MACE, which effectively blocks the diffusion of Ag\(^+\) cations and prohibits porosification to produce low-porosity mp-SiNWs. Less porous mp-SiNWs reduce optical scattering from the porous Si skeletons and vertically protrude from the wafer without aggregation to facilitate optical trapping. Consequently, low-porosity mp-SiNWs effectively reduce the UV–visible reflection loss in the broadband of 300 to 800 nm.

It is a prerequisite to passivate mp-SiNWs with H-termination for further surface modification and optical applications. However, unlike the widely used 40% NH\(_4\)F to passivate Si(111) wafers with H-termination, Si nanowire arrays are intact in HF because of H-passivation but etched in 40% aqueous NH\(_4\)F with a pH of approximately 8 in which F\(^-\) and NH\(_4^+\) ions are dominant. The NH\(_4\)F etching is attributed to F\(^-\) anions nucleophilically attacking Si atoms to terminate Si with F.
atoms. The grafted Si–F bonds have strong dipole moment to significantly polarize and weaken Si back bonds. The etching rate in terms of the NW length is evaluated in the order of \( n^-\text{SiNWs}(100) < n^+\text{-SiNWs}(100) < n^{+2}\text{-mp-SiNWs}(100) < n^{+2}\text{-mp-SiNWs}(111) < n^+\text{-SiNWs}(111) \), which could be explained by three factors: the doping level, the atomic ratio \( F_{1s}/Si_{2p} \), and the stoichiometric \( x \) of the surface termination Si–Fx.

In deoxygenated mesitylene containing 0.2 mol/L DEBZ, mp-SiNWs are monosilylated with DEBZ at a modest temperature of 110°C. The monosilylation creates Si-C=C contacts to immobilize DEBZ and retains the molecular conjugation configuration. Compared to the relatively smooth surfaces of SiNWs, mp-SiNWs appear to have porous surfaces with numerous surface defects that could not be effectively passivated by the grafted monolayers. However, the modified mp-SiNWs with chemically active monolayers will still be facilely subjected to further chemical modification and surface functionalization. In addition, the monosilylation encodes mp-SiNWs with PL of DEBZ, opening the door to flexible engineering of the PL of mp-SiNWs for optoelectronic and bio-detection applications.

9.2 Perspective

9.2.1 Plasmonic enhanced Raman optical activity (ROA)

In Chapter 4, I demonstrated a new method of chirality transfer from chiral host to achiral guest, leading to induced chiroptical activity of achiral guests made of plasmonic materials that are not facilely sculpted in their helical form. The new method effectively broadens the material range of plasmonic chiral nanostructures, to excite nanoplasmons with UV-active chiroptical activity 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, that is, surface-enhanced Raman optical activity (SEROA). This would open a door to the development of chiroptical spectroscopy for sensitive detection of absolute configuration that is of urgent interest in the study of stereobiochemical conformation and bio-interactions that are of crucial, substantial importance to our understanding of a wide range of homochirality-determined biological phenomena.

9.2.2 CPL-induced enantioselective photocyclodimerization

In Chapter 5, ORD could be further used to monitor the photocyclodimerization products of enantiomer (+)-3 and (−)-3. Meanwhile, the ee values of the AC photocyclodimerization mediated by the AgNHs are generally not more than 10%, the weak photocatalytic enantioselectivity is highly probably ascribed to non-polarized irradiation, which markedly reduce the ee value below 25% (Figure 5.7c). Numerical simulation reveals that the irradiation of CPL makes the localized C have one sign over the helical surface, resulting in an ee value of more than 95% (Figure 9.1). The dramatic amplification of ee may effectively enhance the photocyclodimerization enantioselectivity. The CPL-induced photocyclodimerization mediated on the plasmonic NHs is required for further investigation.
Figure 9.1 Schematic of simulated optical chirality $C$ on a LH-AgNH (with a $d$ of 56 nm, $D$ of 186 nm, $H$ of 182 nm, $n$ of 1, $P$ of 126 nm), under RCP irradiation with a wavelength of 365 nm. $e_C$ is evaluated to be 95.4%. The simulation under LCP reveals $e_C$ of $-95.0\%$. 
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Patents

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**Conferences**


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