Two chiroptical modes of silver nanospirals

To cite this article: Fan Bai et al 2016 Nanotechnology 27 115703

View the article online for updates and enhancements.
Two chiroptical modes of silver nanospirals

Fan Bai, Junhong Deng, Mengsu Yang, Junxue Fu, Jack Ng and Zhifeng Huang

1 Department of Physics, Hong Kong Baptist University (HKBU), Kowloon Tong, Kowloon, Hong Kong SAR, People’s Republic of China
2 Institute of Advanced Materials, Hong Kong Baptist University (HKBU), Kowloon Tong, Kowloon, Hong Kong SAR, People’s Republic of China
3 Institute of Computational and Theoretical Studies, Hong Kong Baptist University (HKBU), Kowloon Tong, Kowloon, Hong Kong SAR, People’s Republic of China
4 Partner State Key Laboratory of Environmental and Biological Analysis, Hong Kong Baptist University (HKBU), Kowloon Tong, Kowloon, Hong Kong SAR, People’s Republic of China
5 Department of Biomedical Sciences, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Kowloon, Hong Kong SAR, People’s Republic of China
6 HKBU Institute of Research and Continuing Education, 9F, the Industrialization Complex of Shenzhen Virtual University Park, No.2 Yuexing 3rd Road, South Zone, Hi-tech Industrial Park, Nanshan District, Shenzhen, Guangdong, People’s Republic of China

E-mail: jacktfng@hkbu.edu.hk and zfhuang@hkbu.edu.hk

Received 5 October 2015, revised 7 December 2015
Accepted for publication 18 January 2016
Published 15 February 2016

Abstract
As an emerging three-dimensional chiral metamaterial, plasmonic nanospirals (NSs) possess inherent chiroptical activity that has attracted increasing attention for developing potential photonic applications. However, the study of chiroptical activity of plasmonic NSs is still in its infancy, especially for NSs made of silver, which is a typical plasmonic material with high plasmonic quality. Herein, we present a systematic study of circular dichroism (CD) of silver NSs (AgNSs) that are fabricated and engineered in helical lengths by glancing-angle deposition (GLAD) and dispersed in ethanol. The CD spectrum is composed of a bisignated mode of two peaks, one in the UV regime and the other in the visible. The UV mode has a resonance wavelength saturating at ~375 nm and a linewidth decoupled from the helical elongation, while the visible mode tends to have a redshift and its linewidth broadens linearly with the elongation of AgNS. Helical elongation generally amplifies the chiroptical activity of both modes. Finite-element simulation shows good agreement with the experimental CD results, and accounts for the wavelength-related chiroptical distinction in terms of the resonance wavelength. This work contributes to understanding the bisignated chiroptical responses of plasmonic nanospirals, and introduces a simple method to tailor the visible chiroptical activity that is strongly desired to explore a wide range of chirality-related bio-applications.

Keywords: silver nanospirals, chiroptical activity, circular dichroism, glancing-angle deposition, chiroplasmon

(Some figures may appear in colour only in the online journal)
depend substantially on the chiral morphology of plasmonic materials [2]. When chiral molecules are located in the vicinity of enhanced optical chirality, their chiroptical interaction will be significantly amplified to make their trace detection [3] and the sensitive determination of their absolute configuration easier. It will, consequently, promote a wide range of chirality-related applications in the pharmaceutical industry, agricultural production, food quality monitoring and control, disease diagnosis and treatment, as well as environmental protection and sustainable development.

Different techniques have been developed to create chiroplasmonic structures, including the induction of chiroptical activity in achiral nanoclusters via conjugation with chiral molecules [4–10], collective interaction of achiral nanoparticles that are chirally assembled [11–15], the fabrication of two-dimensional chiral metamaterials [16–18], multi-layer chiral stacking [19–23], and the generation of three-dimensional chiral metamaterials [24, 25]. The last technique typically produces metallic spirals. Microspirals with a helical pitch on the micro-scale typically have chiroptical activity in the IR regime [26], and can be fabricated by direct laser writing [24] and multi-beam holographic lithography [27]. However, these fabrication techniques for microspirals cannot be easily scaled down to the nanoscale due to the optical limitation. Alternatively, metallic NSs can be generated by (1) colloidal nanohole lithography [28], (2) focused ion-beam-induced deposition [29], (3) electron-beam-induced deposition [30] and (4) glancing-angle deposition (GLAD) [25]. The first approach to NS fabrication indispensably involves a set of pre- and post-fabrication processes; the second and third have practical difficulties in large-scale fabrication. In that sense, GLAD is a unique technique for carrying out a for carrying out wafer-scale deposition via a one-step process, and can enable flexible engineering of spiral materials and helical structures [31]. Plasmonic NSs have chiroptical responses in the UV–visible–near-IR spectra [32].

Chiroptical activity can be characterized by circular dichroism (CD), that is, the difference in the extinction of left- and right-handed circularly polarized (LCP and RCP) irradiation in a sample. At present, research into the chiroptical activity of plasmonic NSs is very limited. Ag and Au are the two typical plasmonic materials that have been widely studied. Ag has a higher plasmonic quality than Au [33], such that it is of fundamental importance to study the chiroptical activity of AgNSs. Although Zhao et al started to simulate the chiroptical response of AgNSs theoretically in 2007 [34], it was in 2014 that Krstić et al experimentally demonstrated that AgNSs are chiroptically active in the visible regime [35]. The delay in experimental confirmation is mainly attributed to a lack of appropriate techniques to reliably generate metallic NSs, until in 2013 Fischer et al employed extremely-low-substrate-temperature GLAD to fabricate plasmonic NSs made of Au, Cu and Ag:Cu alloy [25]. Although AgNSs have been engineered in helical lengths to study antenna performance [36], there have been no systematic studies of the chiroptical response of AgNSs. With respect to plasmonic materials, furthermore, the resonant CD wavelength can be tuned over the entire visible spectrum: ∼750 nm for Cu, ∼600 nm for Au and ∼480 nm for Cu–Ag and Ni–Ag alloys [32].

Herein, we employ low-substrate-temperature GLAD to create AgNSs that have CD composed of a bisignated mode of two peaks, one in the UV regime and the other in the visible. Spiral structures are easily tailored by GLAD, to statistically study the effect that the helical elongation has on the bisignated mode. The two chiroptical modes tend to respond distinctly with the helical elongation, and the finite-element method (FEM) is employed to numerically simulate the chiroptical response and explain the wavelength-related chiroptical difference.

2. Materials and methods

2.1. GLAD of AgNSs

In a physical vapor deposition system (JunSun Tech Co. Ltd, Taiwan), Ag powders (99.99%, Lesker) were evaporated at an electron-beam accelerating voltage of 8.0 kV and emission current of 15–25 mA to obtain a deposition rate (Rd) of 0.3 nm s−1 monitored by a quartz crystal microbalance. Ag was deposited on Si wafers (Semiconductor Wafer, Inc.) in an area of 1.5 × 1.5 cm2 without surface pre-patterning, and the substrate temperature was controlled to be ∼2°C using an ethanol cooling system. In a high vacuum of 10−7–10−6 Torr, GLAD was operated at a deposition angle of 86° with respect to the substrate normal. As-deposited Ag was sculptured into helices by slowly rotating the substrates clockwise to generate right-handed helices and in counterclockwise to create left-handed spirals. A spiral can be morphologically characterized by its pitch P, number of pitches n, height H (H = nP), coil diameter D and wire diameter d (inset in figure 1(a)). GLAD enables one to easily control P and n. P (in units of nm per revolution) is engineered by

\[ P = 360 \frac{R_d}{R_s} \]

where Rs is the rate of substrate rotation in unit of degrees per second. In this work, R_d was fixed as 0.067 nm s−1, which was calibrated on the substrate surface with respect to the glancing deposition angle of 86°. n was engineered by the azimuthal angle of substrate rotation (φ): φ of 540° and 720° gives rise to n of 1.5 and 2, respectively.

2.2. Spectral characterization

A Si wafer with as-deposited AgNSs was immersed in 0.1 mol L−1 CTAB (cetyl trimethylammonium bromide) aqueous solution for 3 h, and then was sufficiently rinsed by deionized water (DI water with 18.2 MΩ, Milli-Q reference water purification system fed with campus distilled water) and dried by N2. The treated wafer was transferred into ethanol for 15 min ultrasonication to sufficiently disperse the CTAB-grafted AgNSs in the solvent. Then the solution with dispersed AgNSs was transferred to a standard solution cell with an
2.3. Structural characterization

The as-deposited wafers were mechanically split, leaving the freshly split surfaces for SEM characterization (field emission scanning electron microscopy, Oxford, LEO 1530). Not less than 30 AgNSs characterized by SEM were analyzed to statistically measure the helix structural parameters that have an algebraic average value and standard deviation. For clarity, only the average values are shown in figures 2 and 4. Several drops of ethanol with dispersed CTAB-grafted AgNSs were applied to a lacey carbon film on a grid structure (Electron Microscopy Sciences). The grid was ambiently dried for the TEM characterization (Tecnai G2 20 S-TWIN).

2.4. FEM simulation

The FEM was employed using the commercial software package ‘Comsol Multi-physics’ to simulate CD of individual AgNS, which is elaborated in the supporting information.
3. Results and discussion

GLAD enables one to generate a close-packed, random array of AgNSs on a Si wafer without surface pre-patternning, with control over \( P \) (in the range 100–300 nm), \( n \) (as 1.5 and 2) and spiral handedness (left or right) as shown in figure 1. The deposition appears to be uniform in an area of \( 1.5 \times 1.5 \text{ cm}^2 \) (inset in figures 1(c) and (d)). For easy communication, nL-AgNSs denotes the left-handed spirals with \( n \) pitches, whose mirror images are denoted as nR-AgNSs. The statistical analysis reveals that at a given \( R_d \) and substrate temperature, \( D \) increases linearly with \( P \) and the helical widening slope is fitted as 1.23 \( \pm 0.08 \) (figure 2(a)). \( d \) tends to increase with \( P \), but not in a linear manner (figure 2(b)). It is illustrated that the elongation of \( P \) makes an AgNS become wider (in terms of \( D \)) and thicker (in terms of \( d \)). Note that GLAD of materials with high melting point (such as oxides and semiconductors) usually produces a broadening structure due to the effects of shadowing and competition, that is, \( d \) gradually increases with the helical growth [37]. However, AgNSs have a negligible broadening effect, probably due to the relatively low melting point of Ag. Ag adatoms are apt to diffuse on a helical surface after attaching to an existing spiral, leading to the elimination of the broadening effect. A spiral has a length \( L \) given by

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

AgNSs appear to elongate linearly with \( P \), and the helical elongation slope is fitted to be 4.67 \( \pm 0.57 \) (figure 2(c)).

As monitored by CD (figure 3(a)), dispersed AgNSs have a chiroptical response in the UV–visible regime composed of two peaks with opposite CD sign, separated by \( \sim 400 \text{ nm} \) (figure 3(b)). The CD spectrum flips around the zero-CD axis if the helical handedness is switched. When Ag is sculptured into nanorods without helical chirality (figure S1a), there is no detectable CD (figure S1b), illustrating that AgNSs have chiroptical activity inherently originating from the helical profile. Dispersed AgNSs have an optical absorption in the spectrum at 320–500 nm, independent of the helical structure (figure 3(b)). It is clear that the two CD peaks originate from a bisignated chiroptical mode. The tailoring of spiral structures (in terms of \( P \) and \( n \)) gives rise to a trivial shift in the resonance wavelength of the UV peak but an obvious shift in that of the visible peak (figure 3(b)), indicating that the two chiroptical modes have different chiroptical dependences on spiral structure. Since the variation of \( D \) and \( d \) with \( P \) is correlated, it is not appropriate to study the chiroptical dependence on just one of the structural parameters of the
The helical length $L$ contains the contributions of all the structural parameters (equation (2)), such that it is reasonable to study the chiroptical dependence on $L$ (figure 4). For the UV chiroptical mode, $\lambda_{\text{max}}$, the wavelength at which a CD peak has the maximum ellipticity $I_{\text{max}}$, as marked in figure 3(b)) is irrelevant to $L$ and fluctuates in a small range of 360–380 nm (figure 4(a)). $I_{\text{max}}$ tends to increase with $L$ but not in a linear manner (figure 4(b)); its full width at half maximum (FWHM) fluctuates in the range 30–70 nm and decouples from $L$ (figure 4(c)), analogously to $\lambda_{\text{max}}$. On the other hand, for the visible mode $\lambda_{\text{max}}$ tends to redshift linearly with $L$, and the redshift slope is fitted as $0.15 \pm 0.02$ (figure 4(d)); $I_{\text{max}}$ tends to increase with $L$ (figure 4(e)), analogously to figure 4(b); its FWHM also increases linearly with $L$, and the linewidth widening slope is fitted to be $0.18 \pm 0.02$ (figure 4(f)). It is illustrated in figure 4 that, although the helical elongation generally amplifies the chiroptical activity of the two chiroptical modes, one mode differs from the other. The UV mode has the resonant $\lambda_{\text{max}}$ and linewidth decoupling from the helical elongation. In contrast, the visible mode tends to linearly redshift and spectrally widen with the helical elongation, consistent with the visible chiroptical mode of copper NSs [38] and the numerical simulation [39]. Induced by the helical elongation, analogously, the Ti–Ag alloy NSs chiroptically active in the visible regime have a redshift of resonance wavelength [40], and the chiroptical response of microspirals [24] and NSs [25] composed of Au is amplified.

To understand the chiroptical distinction in the two modes, CD of dispersed AgNSs is numerically simulated by FEM. The dispersed AgNSs have random orientation in the solvent (figure 3(a)), such that the orientational average CD of a single AgNS is calculated by performing an integration over all solid angles in terms of the polar angle $\theta$ and azimuthal angle $\varphi$ (figure S3b). The simulated CD spectra of a 2L-AgNS and 2R-AgNS are in good agreement with experiment in the range 300–600 nm (figure 5). There is an additional peak simulated at 600–700 nm, probably due to the deviation of the simulation from the experiment in terms of spiral structure and dielectric constant. The as-deposited AgNSs inevitably have structural irregularity and inhomogeneity, and the dielectric constants used in FEM (figure S3a) may deviate from the actual values of the as-deposited samples. It is difficult to incorporate these details into the simulation. However, the good agreement in figure 5 shows that the FEM simulation does capture the chiroptical essence of dispersed AgNSs.

![Figure 4.](image) The dependence of chiroptical activity on helical length ($L$): (a)–(c) the UV chiroptical mode; (d)–(f) the visible chiroptical mode. (a), (d) $\lambda_{\text{max}}$, (b), (e) $I_{\text{max}}$, and (c), (f) FWHM plotted versus $L$, with the legend shown in (a), (d), (f). The plot is linearly fitted by the black line; (b), (e) a thick arrow shows that $I_{\text{max}}$ tends to increase with $L$, but not in a linear manner.

![Figure 5.](image) CD spectra of 2L (in solid red) and 2R (in solid blue) AgNSs with $P$ of 230 nm, which are simulated by FEM (dashed lines).
The chiroptical distinction can be understood in terms of the resonant wavelength $\lambda_{\text{max}}$. UV light has a smaller extinction coefficient than visible irradiation and can extend further into the metal. Hence, $\lambda_{\text{max}}$ of the UV mode tends to saturate and consequently decouple from helical structures [41]. On the other hand, the visible light has a larger extinction coefficient and is preferentially scattered by AgNSs. It is simulated by FEM that in the visible regime, the extinction coefficient saturate and consequently decouple from helical structures (figure 6). As a result, the visible $\lambda_{\text{max}}$ has a linear red-shift with the elongation of AgNS, but is independent of $d$ (figure S4).

4. Conclusion

Chiral AgNSs are fabricated and simply tailored in the helical structures using GLAD, and exhibit chiroptical activity inherently originating from the helical structure. Dispersed AgNSs have a chiroptical response composed of the UV and visible chiroptical modes that are bisignated in the CD spectrum. Helical elongation generally amplifies the chiroptical activity of the two modes. The resonant wavelength of the UV mode saturates at $\sim$375 nm, and its linewidth is independent of the spiral elongation. In contrast, the visible mode redshifts and spectrally widens with the helical elongation in a linear manner. The FEM simulation is in good agreement with the experimental CD result, and accounts for the chiroptical difference with respect to the resonant wavelength. The UV irradiation is mainly absorbed in AgNSs, resulting in the saturation of the UV resonant wavelength. On the other hand, the visible irradiation is preferentially scattered by AgNSs and the optically excited electric field flows along the longitudinal axis of the coil, leading to the linear redshift of the visible resonant wavelength with the helical elongation. This work contributes to our understanding of the bisignated chiroptical responses of AgNSs, and the creation of a simple method to tailor the visible chiroptical activity as strongly desired for developing a wide variety of potential applications in enantiomer differentiation, enantioselection, chiral catalysis, enantiomer trace detection and bioimaging.

Acknowledgments

The authors acknowledge Mr Benson Leung (Physics, HKBU) for his technical assistance in TEM (funded by SEG_HKBU06) and Mr Edward Chan (Physics, HKBU) for his technical support in x-ray diffraction. This work was financially supported by HKBU8/CRF/11E (GLAD; FB), NSFC/21473149 (FB, JHD), SKL14-15_P004 (FB), FRG2/13-14/018 (FB), NSFC/11304260 (JN) and FRG2/13-14/081 (JHD, JN).

Notes

The authors declare no competing financial interest.

References


[34] Zhang Z Y and Zhao Y P 2007 Optical properties of helical Ag nanostructures calculated by discrete dipole approximation method Appl. Phys. Lett., 90 221501


[40] Larsen G K and Zhao Y 2014 Extracting the anisotropic optical parameters of chiral plasmonic nanostructured thin films using generalized ellipsometry Appl. Phys. Lett., 105 071109