

Predicting the Optical Asymmetry of Cholesteric Liquid Crystals Templated Gold Nanorods Helical Assemblies

Xiyang Wei¹, Yongguang Chen¹, Yi Yang^{1,*}, Yang Liu^{1,*}

1. College of Information Science and Technology, Donghua University, 2999 North Renmin Road, Songjiang District, Shanghai 201-620, China.

Abstract

The incorporation of nanomaterials into liquid crystal (LC) hosts presents a distinctive opportunity to examine the self-assembly of nanomaterials and to augment the functional capabilities of the LC host. The incorporation of gold nanomaterials in liquid crystal (LC) hosts is currently the subject of significant attention in the scientific community, and has a variety of applications, including optical information entropy, signal modulation, chiral molecule recognition and so forth. In this research, a theoretical approach is proposed for the prediction of the optical asymmetry of gold nanorods (Au-NRs) helical assemblies in a cholesteric liquid crystal (CLC) host based on their extinction performance. The findings of this research will provide a simplified and accessible means for researchers in various fields to relate to the optical asymmetry of Au-NRs helical assemblies.

Author Keywords

Chiral Nanoparticles, Gold Nanorods, Optical Asymmetry

1. Introduction

Chirality represents a fundamental property of matter, manifesting as a natural phenomenon in numerous biological and chemical systems [1]. In recent years, chiral plasma nanostructures have attracted considerable attention and become a prominent research topic in numerous fields due to their notable light-matter interaction [2]. Chiral plasma nanostructures, particularly noble metal nanomaterials (gold and silver), have demonstrated considerable potential for application in a range of fields, including biosensing [3], photocatalysis [4], and photothermal therapy [5], due to their pronounced surface plasmon resonance (SPR) effect resulting from interaction with electromagnetic waves within the visible light spectrum. Anisotropic plasma nanomaterials, particularly gold nanorods, exhibit dual SPR peaks along the horizontal and vertical axes, designated as TSPR and LSPR, respectively. In comparison to isotropic metal nanoparticles, gold nanorods demonstrate an adjustable LSPR peak and an enhanced electromagnetic field [6].

Over the past few decades, a number of methods have been reported for the manufacture of chiral gold nanorods, including photolithography and chemical synthesis [7], resulting in a diverse range of compositions, morphologies, and sizes. These studies have contributed to our understanding of the morphological details of chiral gold nanorods. However, the lack of comprehension of the associated chiral-induced growth mechanism has resulted in constrained control over the morphological details, consequently limiting the ability to regulate the final optical activity. Despite the existence of theoretical models that elucidate the relationship between chiral morphology and the optical activity of gold nanorods [8-9], there remains a paucity of existing studies and a dearth of corresponding theories that can inform the selection of the optimal optical activity in the context of chiral morphology.

To gain a deeper understanding of the optical asymmetry of gold nanorods (Au-NRs) helical assemblies, a theoretical analysis was conducted between their extinction characteristics and g-factors. We believe the research output presented here will prove beneficial in further investigations of Au-NRs helical assemblies with regard to their potential applications in the field of optical information entropy, signal modulation, chiral molecule recognition and other related areas.

2. Experimental

The FDTD method (8.19.1584 for x64, Lumerical FDTD Solutions, Canada) was employed to obtain the Extinction spectra, CD spectra and g-factor of Au-NRs. The nanorod geometry is the rounded cylinder model in FDTD object library, with 56nm in length and 15nm in diameter. In these simulations, the experimental data of CRC was used to model the complex permittivity of Au. The simulation environment was set using the refractive index of E7 liquid crystal ($n=1.634$), and set the mesh size to 2 nm. The Au-NRs were illuminated by left/right-handed circularly polarized light (CPL), which consisted of two total-field scattered-field (TFSF) sources, which were set in the range of 400 to 1600 nm, with a phase difference of 90° for left-handed CPL (LCP) and -90° for right-handed CPL (RCP). Two analysis groups consisted of a box of power monitor were used to calculate the absorption and scattering spectra.

3. Results and Discussion

We have demonstrated the successful preparation of strip and helical assemblies in a LC host [10], and have also presented preliminary findings on the optical asymmetry of Au-NRs helical assembly in a CLC host. To further elucidate and enhance the discourse and characterization of optical asymmetry in Au-NRs helical assemblies, additional simulations have been conducted on Au-NRs helical assemblies with varying aspect ratios and pitches. The findings are presented in the subsequent Figure 1 and 2.

The Au-NRs helical assemblies were constructed from 5 to as many as 18 Au-NRs. As illustrated in Figure 1, the longitudinal-localized surface plasmon resonance (l-LSPR) signal and the transverse-localized surface plasmon resonance (t-LSPR) signal in extinction spectra exhibited a blue-shift upon additional insertion of Au-NRs in helical assemblies, accompanied by a gradual increase in amplitude. It is noteworthy that the resulting prominent l-LSPR in the extinction spectra remained at near-infrared wavelengths, while the t-LSPR absorption signal exhibited a less pronounced blue shift. This suggests that the Au-NRs helical assemblies exhibit excellent extinction at NIR wavelengths. Concurrently, although the degree of blue-shift and peak change varies according to the aspect ratio and pitch of the Au-NRs, as illustrated in Figures 1a-d, this does not impact the overall optical asymmetry of the helical structure of Au-NRs.

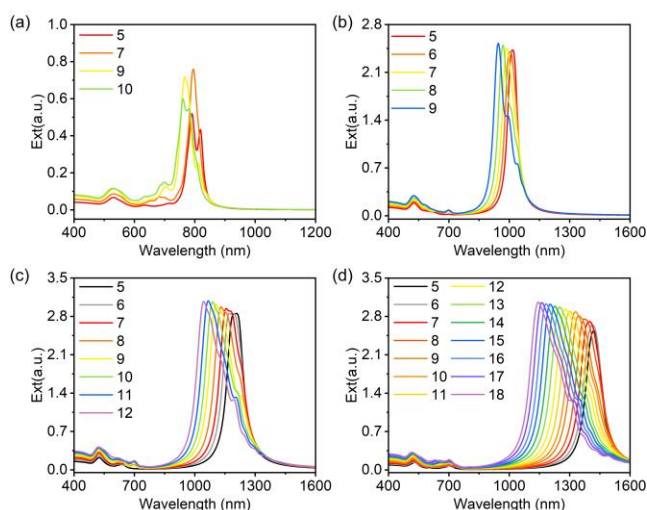


Figure 1. Extinction spectra of Au-NRs helical assemblies at different pitches. (a) 2.5 aspect ratio, 252.93 pitch (b) 3.9 aspect ratio, 283.78 pitch. (c) 5.05 aspect ratios, 351.64 pitch. (d) 6.73 aspect ratios, 407.16 pitch.

The variation of helical assemblies of Au-NRs has a significant impact on the interaction between light and Au-NRs, as evidenced by changes in both the extinction spectrum and the asymmetry g -factor. It was observed that the helical assemblies of Au-NRs began to exhibit discernible g -factor signals at the point where the number of Au-NRs in the helical assemblies reached 6. This phenomenon can be attributed to the fact that the helical structure, comprising a limited number of Au-NRs, exhibits only a minimal degree of chiral activity. Consequently, it does not manifest a pronounced optical asymmetry when subjected to circularly polarized light. However, it was also observed that the intensity of the bisignate g -factor signals increased and the wavelength blue-shifted, which is consistent with the variation rules of t-LSPR and l-LSPR in the extinction spectrum.

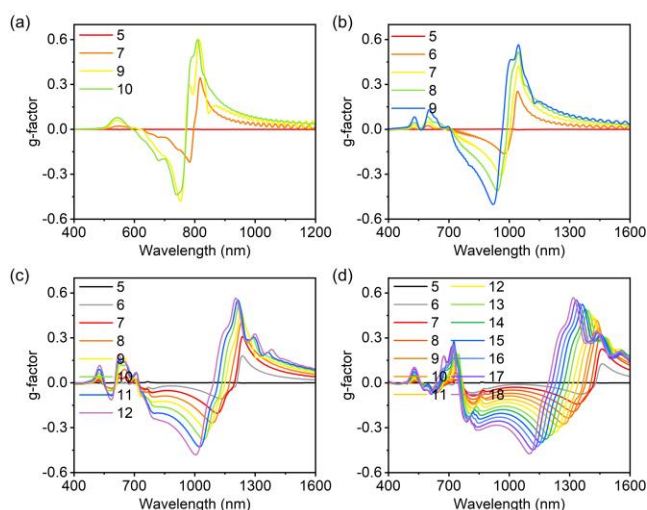


Figure 2. g -factor of spiral structures of gold nanorods with different aspect ratios at different pitches. (a) 2.5 aspect ratio, 252.93 pitch (b) 3.9 aspect ratio, 283.78 pitch. (c) 5.05 aspect ratios, 351.64 pitch. (d) 6.73 aspect ratios, 407.16 pitch.

In light of this correlation, it is postulated that the characteristic

parameters of the extinction spectrum, such as peak position and amplitude, can serve as effective predictors for the construction of a model to estimate the g -factor. By defining a parameter, the relationship between the magnitude of the g -factor and the optical activity of helical assemblies of gold nanorods can be elucidated, thus facilitating the qualitative evaluation of their optical asymmetry. This hypothesis is supported by observations indicating that while the degree of blue shift and peak changes vary due to differences in aspect ratios and pitches of the Au-NRs, these variations do not affect the change rules of the overall optical asymmetry of the helical structure. The prominent LSPR signals in the near-infrared region and the relatively stable T-LSPR further validate the robustness of this relationship. The extinction spectrum thus provides insights not only into the plasmonic properties of the Au-NRs helical assemblies, but also offers a reliable framework for predicting the g -factor, thereby paving the way for the reasonable definition of an optical asymmetry formula.

The extinction of Au-NRs is inherently anisotropic in both the longitudinal and transverse directions. Our previous study demonstrated that reducing the distance between Au-NRs and incorporating the additional Au-NRs in helical assemblies resulted in a decrease in the longitudinal extinction signals and an increase in the transverse extinction signals, as well as the increase in CD signals and g -factors. We believe the anisotropy in the extinction of Au-NRs is an essential sign to understand the chiral characteristics of Au-NRs and their assemblies, and here we determine an extinctive anisotropy factor (Δe) of Au-NRs and their assemblies as followings to evaluate their chiral characteristics,

$$\Delta e = 1 - \frac{|e_L - e_T|}{e_L + e_T} \quad (1)$$

where e_L is the intensity of longitudinal extinction signal, and e_T is the intensity of transverse extinction signal. Therefore, when the Au-NRs are longitudinally perpendicular to the polarization direction of the incident light, it means that in the extinction spectra $e_L > e_T$, we will have

$$\Delta e = \frac{2e_T}{e_L + e_T} \quad (2)$$

and when the Au NRs are longitudinally parallel to the polarization direction of the incident light, it means that in the extinction spectra $e_T > e_L$, we will have

$$\Delta e = \frac{2e_L}{e_L + e_T} \quad (3)$$

Δe ranges between 0 and 1, with values approaching 1 indicating significant extinction anisotropy in Au-NRs. To further assess the general applicability of the proposed Δe in characterizing chiral properties, simulations were conducted for 29 Au-NRs with varying aspect ratios and their respective helical assemblies within a cholesteric liquid crystal host under different pitches, examining their extinction (Ex), circular dichroism (CD), and g -factor characteristics. At the same time, Figure 3 further shows the resulting relationship between Δe and the asymmetric g -factor. The simulation results reveal that, for both Au-NRs with different aspect ratios and their helical assemblies, an increase in optical asymmetry correlates with a rise in the asymmetric g -factor for

each pitch, aligning closely with our expectations. This suggests that $\Delta\epsilon$ is both general and versatile, extending its applicability to the characterization of optical asymmetry in c-Au-NRs, and we always have

$$g\text{-factor} \sim \Delta\epsilon = 1 - \frac{|e_L - e_T|}{e_L + e_T} \quad (4)$$

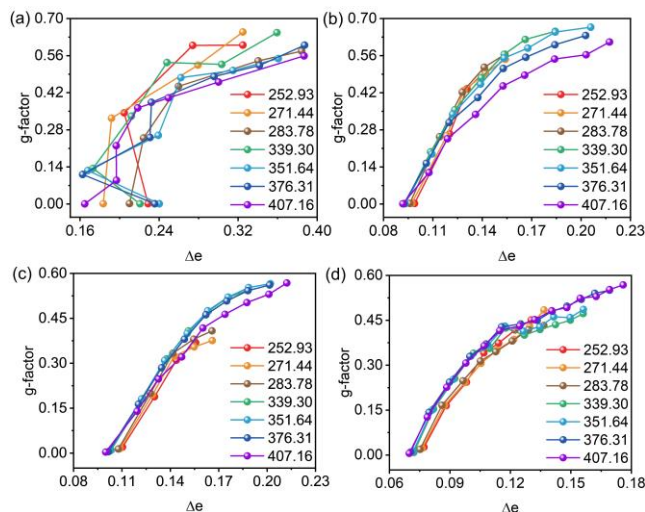


Figure3. Optical asymmetry curves of spiral structures of gold nanorods with different aspect ratios at different pitches. (a) 2.5 aspect ratio. (b) 3.9 aspect ratio. (c) 5.05 aspect ratios. (d) 6.73 aspect ratios.

As illustrated in Formula 4, an optical asymmetry formula exhibiting a positive correlation with the asymmetric g-factor has been established through the utilization of the characteristic parameters of the extinction spectrum. This work not only defines a quantitative relationship but also validates its applicability and generalizability within the scope of the present study. It is important to acknowledge certain limitations of this study. Despite the extensive simulations conducted, the finite number of cases explored means that not all possible combinations have been exhaustively covered. The formula is currently applicable to helical assemblies of Au-NRs with 29 distinct aspect ratios, ranging from 2.5 to 7.77, and seven pitches, spanning 252.93 nm to 407.16 nm. Nevertheless, it is believed that the formula can be extended to other aspect ratios and pitches beyond those investigated. Furthermore, as the influence of external environmental conditions on the structure was not extensively considered in this study, the formula is not applicable to scenarios where changes in the overall helical structure of Au-NRs occur due to external perturbations. Further research is required to address these limitations and enhance the robustness of the proposed formula.

4. Conclusion

In conclusion, based on the extinction spectrum of Au-NRs helical assemblies, we propose a theoretical formula to predict the optical asymmetry of the Au-NRs helical structure in a CLC host. A comprehensive examination of the optical response of the simulated Au-NRs helical structure, encompassing both the extinction spectrum and the asymmetric g-factor, unveiled a consistent pattern in the variation of these parameters. This led to the formulation of an optical asymmetry equation that employs

the distinctive peaks of t-TSPR and l-LSPR within the extinction spectrum to predict the g-factor and evaluate optical asymmetry. Furthermore, the formula has been validated through extensive simulations, which have revealed a strong positive correlation between the defined formula parameter $\Delta\epsilon$ and the g-factor, thus demonstrating the applicability and generalizability of the formula. In conclusion, we examine the particular area of application of the formula, acknowledge its current limitations, and suggest avenues for future research to extend its applicability and enhance its robustness.

5. Acknowledgements

Yang Liu acknowledges the financial support from the National Natural Science Foundation of China (62241503), the Natural Science Foundation of Shanghai (22ZR1401400).

6. References

- [1] C. L. Hao, R. Gao, Y. Li, L. G. Xu, M. Z. Sun, C. L. Xu, and H. Kuang. "Chiral Semiconductor Nanoparticles for Protein Catalysis and Profiling." *Angewandte Chemie* 58(22), 7371-7374(2019).
- [2] P. Cintas. "On Chirality and the Universal Asymmetry. Reflections on Image and Mirror Image. By Georges H. Wagnière," *Angewandte Chemie International Edition*. 46(48), 9143-9144(2007).
- [3] J. Q. Liang, P. P. Guo, X. J. Qin, X. H. Gao, K. Ma, X. F. Zhu, X. Jin, W. W. Xu, L. X. Jiang, and P. F. Duan. "Hierarchically Chiral Lattice Self-Assembly Induced Circularly Polarized Luminescence," *ACS Nano* 14(3), 3190-3198(2020).
- [4] R. B. King. "Chirality and handedness: the Ruch "shoe-potato" dichotomy in the right-left classification problem," *Annals of the New York Academy of Sciences* 988, 158-170(2003).
- [5] M. Hentschel, M. Schäferling, X. Y. Duan, H. Giessen, and N. Liu. "Chiral Plasmonic," *Science Advances* 3(5), e1602735(2017).
- [6] X. P. Sun, H. J. Kong, Q. H. Zhou, S. J. Tsunega, X. L. Liu, H. F. Yang, and R. H. Jin. "Chiral Plasmonic Nanoparticle Assisted Raman Enantioselective Recognition," *Analytical Chemistry* 92(12), 8015-8020(2020).
- [7] N. N. Zhang, Z. L. Shen, S. Y. Gao, F. Peng, Z. J. Cao, Y. Wang, Z. Wang, W. Zhang, Y. Yang, K. Liu, and T. Sun. "Synthesis and Plasmonic Chiroptical Properties of Double-Helical Gold Nanorod Enantiomers," *Advanced Optical Materials* 11(18), 2203119(2023).
- [8] M. Obelleiro-Liz, V. F. Martín, D. M. Solís, J. M. Taboada, F. Obelleiro, and L. M. Liz-Marzán. "Influence of Geometrical Parameters on the Optical Activity of Chiral Gold Nanorods," *Advanced Optical Materials* 11(18), 2203090(2023).
- [9] W. W. Fu, J. Q. Chen, S. P. Zhang, G. C. Zheng, and Y. Zhang. "Discrete and dimeric chiral plasmonic nanorods: intrinsic chirality and extrinsic chirality," *Journal of Materials Chemistry C* 12(25), 9139-9145(2024).
- [10] Y. Liu, G. J. Lin, Y. G. Chen, X. Y. Wei, M. J. Du, Y. F. Zhang, Z. L. Li, L. N. Zhao. "UV-Triggered Optical Asymmetry Modification of Gold Nanorods Helical Assemblies in a Cholesteric Liquid Crystal Host," *Advanced Optical Materials* 12(24), 2400862(2024).