DOCTORAL THESIS

Study on the Optical Properties of Chiral Inorganic Nanomaterials and Their Interactions with Molecules and Bacteria

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ABSTRACT

Chiral inorganic materials can be considered highly promising candidates for a broad array of transdisciplinary applications because of their unique properties and interactions with optical, biological and chemical systems. These distinct chirality of these materials enables them to interact selectively with chiral molecules and structures, leading to enhanced functionality and performance. Chiral inorganic materials have shown promise in optical performance, such as circular dichroism (CD) and circularly polarized light emission (CPLE). The unique properties and versatility of chiral inorganic materials make them promising candidates with significant potential for advancing various scientific and technological transdisciplinary fields.

In chapter 1, the concept of chirality is explored from various perspectives, providing a comprehensive introduction to this fundamental concept. The chapter also delves into the principles of CD and CPLE, explaining their significance in the context of chiral materials. Both chiral organic and inorganic materials are discussed, with a detailed focus on the synthesis methods and diverse transdisciplinary applications of chiral inorganic nanomaterials. This chapter lays the groundwork for understanding the intricate properties and potential transdisciplinary uses of chiral inorganic nanomaterials in scientific and industrial fields.

In chapter 2, glancing angle deposition (GLAD) is detailed introduced, which was used to fabricate different chiral inorganic materials for following transdisciplinary researches, including CPLE, manipulating symmetry breaking of organic molecules, and combatting bacteria. Structural engineering about chiral inorganic materials is used

for regulating the optical characteristics of nanostructures, which hold significant fundamental and practical importance in nanoscience and technology.

In chapter 3, in optical filed, CPLE holds potential for applications in three-dimensional displays, data storage, and biometric systems. Nevertheless, the practical implementation of these applications is hindered by the low purity of circular polarization, specifically the small optical dissymmetry factor g_{CPLE}. In this context, GLAD has been employed to fabricate inorganic nanohelices (NHs) that produce CPLE with significantly enhanced g_{CPLE} values. Ceria NHs generate ultraviolet–blue CPLE with a g_{CPLE} of ≈0.06 at a P of ≈830 nm, representing a 10^3-fold increase compared to a P of ≈110 nm. Similarly, CdSe NHs produce red CPLE with a g_{CPLE} of 0.15 at a helical pitch (P) of ≈570 nm, which is 40 times greater than the g_{CPLE} at a P of ≈160 nm. Numerical simulations suggest that the considerable g_{CPLE} values result from the combined effects of photoluminescence and scattering among the densely packed NHs. The GLAD-based NH-fabrication method allows to produce CPLE with tunable colors and substantial g_{CPLE} of 10^{-2}–10^{-1}, facilitating the advancement towards commercial CPLE devices.

In chapter 4, nanostructure engineering was investigated systematically to enrich chiral inorganic materials' application research in biochemistry filed: a wide range of inorganics composed of chiral lattices at their surfaces are reported to manipulate the symmetry breaking of racemic polycyclic aromatic nitrogen heterocycles (PANHs). A series chiral nanoparticles (CNPs) and chiral thin films (CTFs) are fabricated by GLAD, which are selected to act as a chiral stimulator to trigger and manipulate the symmetry breaking of PANHs, including 2-A[4]H and 4-A[4]H. Helicenes undergo symmetry breaking after aggregate on a densely arranged array of CNPs and CTFs, and the homochiral conformations of helicene aggregates are reliably manipulated with the handedness of CNPs and CTFs, monitored with electronic circular dichroism (ECD or CD). The symmetry breaking of helicenes can be generally manipulated by atomically chiral inorganic surfaces made of silica, titanium oxides, iron oxides, tin oxides and gold (Au), which have high surface energy with a DMF contact angle $< 22°$. Low surface energy (with a DMF contact angle $> 40°$) causes stochastic or no symmetry breaking of helicenes at the atomically chiral surfaces of copper oxides, silver (Ag), aluminum oxides, nickel oxides, and cobalt oxides. The enantiospecific interaction of the helicene N-terminals and atomically chiral surfaces plays a critical role in the manipulation of symmetry breaking. This research showed the controllable symmetry breaking to manipulate the homochiral conformations of helicene aggregates, which can help people understand the extraterrestrial origin of the enantiopreference on Earth.

In chapter 5, chiral inorganic nanomaterials were found to hold potential for combating bacterial infections owing to their exceptional biocompatibility and facile surface modification. The antibacterial properties of chiral silica nanosprings (NSs) and achiral tilt silica nanorods (NRs) fabricated via the GLAD method were studied. Characterization techniques including plate counting, live/dead staining, and SEM analysis were employed. Results demonstrated that chiral silica NSs exhibited superior antibacterial efficacy against *Escherichia coli* (*E. coli*) compared to achiral silica NRs.

Furthermore, RH silica NSs showed enhanced antibacterial effects over LH silica NSs. Contact angle and surface energy analysis highlighted the advantageous properties of chiral silica NSs for antibacterial applications. These finding underscored the significance of interfacial stereochemistry in biosystems and suggested the potential for developing tailored chiral functional nanomaterials for targeted biological and medical applications.