Chiral semiconductor photonic thin film with tunable circularly polarized luminescence

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Summary: Inorganic nanowires and semiconductor quantum dots are co-assembled into chiral photonic crystals, generating circularly polarized luminescence with a significant dissymmetry factor and tunable peak position, intensity and sign by controlling the photonic crystals' bandgap, pitch number, and handedness.

Circularly polarized light has many important applications in photonic technologies.[1] Conventionally, circularly polarized luminescence (CPL) is generated from non-polarized light through a linear polarizer and a quarter-wave plate, inevitably inducing the energy loss and increasing the cost.[1] Direct generation of CPL from chiral luminescent materials is efficient and cost-effective, holding the promises for future applications in optical display, chiral synthesis, bio-imaging, information encryption, and quantum communication.[1]

Chiral organic luminescent molecules, lanthanide complexes, polymers, and supermolecules with CPL properties have been used for display and lighting technologies.[2] However, their synthesis is often time-consuming, requires elaborate molecular design, and lacks precise property control, thus limiting practical applications. CPL-active inorganic materials such as QDs and perovskites are promising alternatives to organic materials due to their strong and adjustable photoluminescent properties.[3-5] There are two typical strategies to fabricate inorganic chiral luminescent materials: chiral ligand-mediated synthesis[6] and chiral template (peptide and DNA) assisted assembly.[7] However, the former suffers from low CPL activity due to the inefficient chirality transfer from chiral ligands, and the latter is limited to specific materials due to the required selective binding or size matching with the templates. Incorporating luminophores into supramolecular chiral photonic crystals produces helical structures with a one-dimensional periodicity and strong chiral optical properties, while the lack of control over the photonic bandgap inhibits tunability of CPL properties.[8]

It is well known that the cuticle of the scarab beetles selectively reflects left-circularly polarized light, a phenomenon that has recently inspired Tang et al. to assemble colloidal inorganic nanowires into biomimetic chiral photonic crystals with tunable handedness and photonic bandgap.[9] By co-assembling $NiMoO_4 \bullet xH_2O$ nanowires and CdSSe@ZnS core-shell QDs using the Langmuir-Schaefer process, they produced luminescent inorganic chiral photonic crystals with intense and tunable CPL activities (Figure 1a).[10] Both nanowires and QDs were uniformly aligned in the thin film with a thickness of 20 nm (Figure 1b), and the angle (α=360º/L (L: layer number)) between neighboring layers can be well manipulated to generate chiral photonic crystals with variable pitches (p) (Figure 1c). Thanks to the negligible absorption in the visible region of the $NiMoO_4 \bullet xH_2O$ nanowires, the chiral optical properties are dominated by the diffraction from the chiral photonic crystals, enabling the precise control over the circular dichroism (CD) peak by tuning the photonic bandgap (λ=np, (n: average refractive index)).

The generation of significant CPL requires a good match between the CD and luminescence peak positions, inducing the effective coupling between the photonic bandgap of chiral photonic crystals and the luminescence of QDs. The team fabricated three chiral photonic crystals with the same pitch number of 10 but different pitch lengths (240, 260, and 320 nm), combined them with QDs with luminescence peaks matching the photonic bands, and produced strong CPL with blue, green, and red colors. All CPL peaks showed narrow full width at half maximum of less than 30 nm (Figure 1d). Further, they show that the CPL intensity can be well controlled by the pitch number, and increasing the pitch number enhances the CD and CPL intensity as well as the absolute dissymmetry factor $|g_{lum}|$ thanks to the more significant bandgap effect (Figure 1d, e).

Since the luminescence polarization of QDs depends on the photonic bandgap of the chiral photonic crystals, the team systematically studied this effect by fabricating blue-emitting QDs-doped left-chiral photonic crystals with tunable pitches. The effective coupling between the photonic bandgap and the luminescence of QDs was found to depend on the spectral overlap between CD absorbance and luminescence, with negligible CPL signals from minimal overlapping and strong CPL signals from perfect matching. Furthermore, the off-centering of photonic bandgap from the luminescence peak induced peak shifts of g_{lum}, and the slight blueshift of photonic bandgap relative to the luminescence peak induced the blueshift of g_{lum}, and vice versa. The team conducted theoretical calculations to understand the origin of CPL modulation and found that the

chain structure of QDs induced the parallel transition of dipole moment along the nanowire alignment, influencing the effective coupling between luminescence and photonic bandgap. Quantitative simulation is expected to fully unravel the mechanism of the chiral photonic bandgap effect on the modulation of luminescence polarization.

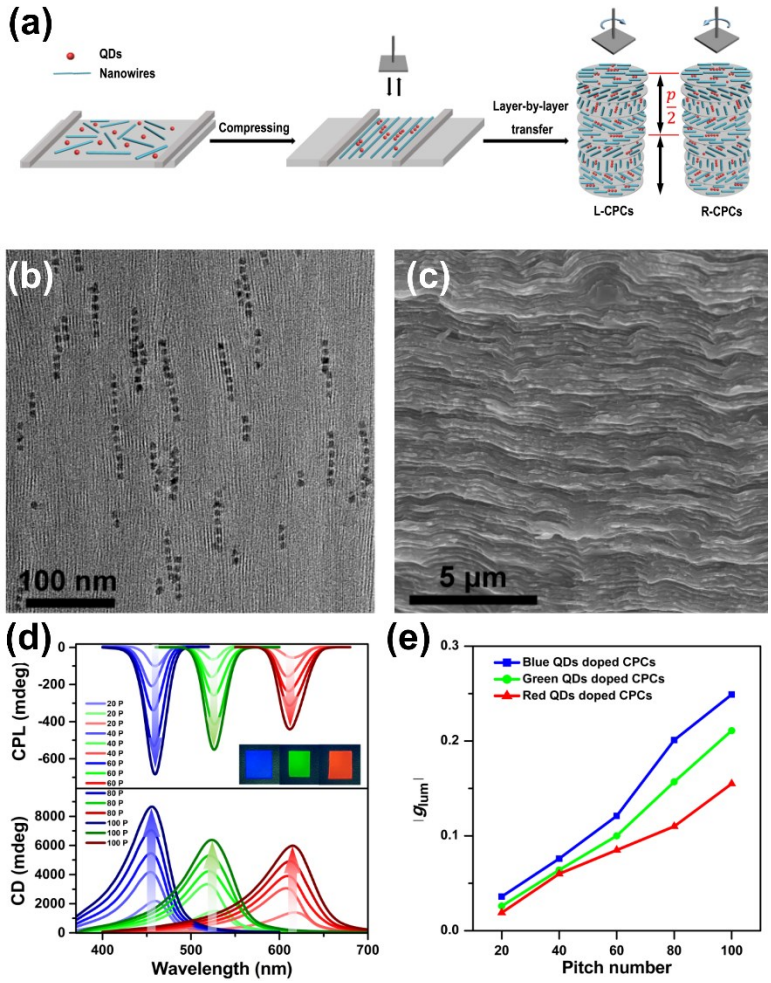

Figure 1. Tunable CPL from the chiral photonic crystals doped with QDs. (a) Schematic illustration of fabricating chiral photonic crystals through layer-by-layer Langmuir-Schaefer co-assembly of colloidal nanowires and QDs. (b) TEM image of a single layer film. (c) SEM image showing the cross-section of QD-doped chiral photonic crystals. (d) CD and CPL spectra of the QD-doped chiral photonic crystals with different pitch numbers. (e) The $|g_{lum}|$ value as a function of the pitch number.

The strategy reported by Tang et al. holds great promises for creating luminescent chiral photonic crystals that can exhibit significant CPL with a tunable sign, position, and intensity. It is expected

to be conveniently extended to assembling nanowires of different luminescent materials into chiral photonic crystals as the Langmuir-Schaefer deposition is a general process. While it is believed to greatly enrich the candidate materials and toolbox for CPL generation, this layer-by-layer approach has its intrinsic limit in the production efficiency. In addition, it requires considerable technical experience before one can successfully fabricate high-quality samples in a reproducible manner. In this regard, there is plenty of room for future research to simplify or automate the assembly process and improve efficiency. An open question is how the assembly defects, such as the misalignment of one or more layers or the introduction of a layer of inconsistent thickness, affect the emission. A systematic study of defect propagation may not only help improve the robustness of the process but also allow the development of new ways to manipulate the CPL properties. Another interesting possibility for the further development of this strategy is to incorporate chirality into photonic crystals with dynamically tunable bandgap, which may enable real-time modulation of CPL properties for many intriguing applications such as sensors and actuators.

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Declaration of Interests:

The authors declare no competing interests.

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