



Helically deployed Au nanoparticles using block copolymer templates as chiral plasmonic monoliths

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This work aims to fabricate polymeric thin films with helically deployed gold (Au) nanoparticles by using self-assembled chiral block copolymers (BCPs*) with controlled helicity as templates, giving polymeric monolith with unique optical properties as chiral plasmonic thin film. Enantiomeric polylactide-based BCPs*, polystyrene-block-poly(*L*-lactide) (PS-*b*-PLLA) and poly-styrene-block-poly(*D*-lactide) (PS-*b*-PDLA) with disulfide junction are designed and synthesized, denoted as PS-ss-PLLA and PS-ss-PDLA, respectively. The helically deployed chemical junctions of the PS-ss-PLLA and PS-ss-PDLA thin films from the self-assembly of helix-forming BCPs* can give thiol end groups preferentially arranged in a one-handed helical fashion at the inner wall of nanoporous PS after hydrolysis of polylactide followed by reducing the disulfide into thiol. Au nanoparticles (Au NPs) with a size of 2-5 nm, resulting from reduction, can associate with the thiol end groups in the nanoporous PS, forming a helical disposition of Au NPs with specific handedness. As a result, circular dichroism (CD) signals of localized surface plasmonic resonance (LSPR) originating from the helical Au NP arrays with preferred chirality can be acquired from the polymeric monolith fabricated, giving appealing applications as chiroptical devices.

1 Introduction

Chirality transfer originates from molecular chirality, giving a preferred helicity of the intra- and inter-chain chiral interactions, and thus transmitting its handedness to the hierarchical levels from self-assembly at different length scales. Many systems have

been studied to utilize chirality transfer for delicate structures, such as lipid membranes, [1] liquid crystals, [2] biomolecules [3–7], supermolecules [8,9] and block copolymers (BCPs). [10–15] While the self-assembled microstructures have drawn great attention, there is lack of detailed studies how the molecular chirality interacts at the mesoscale. Specifically, chiral block copolymers (BCPs*) are well-known for their possibilities of self-assembling into various chiral structures through chirality transfer. Recent studies demonstrate that the junctions between

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the two blocks in diblock copolymers may follow a helical contour at the interface of microdomains, as depicted by an orientational Self-Consistent Field Theory. [16,17] Experimentally, a chromophore was selected as a junction, and a BCP* was synthesized for self-assembly, showing the circular dichroism (CD) signals from inter-chain chiral interaction at the microphase-separated interface. [12] Interestingly, the chromophore can retain chiral arrangement even after removing the minor block, also known as chirality memory effect. [18–20] However, the application of chirality at the interface is limited by the choice of functional groups used as junctions in syntheses. Alternatively, templated syntheses open a path for junction engineering. After removal of a constituent block, the junction can be exposed, making it easier to modify the functional groups after self-assembly. Most interestingly, with the memory at the interface, the helical arrangement of junctions can still be well preserved.

With delicate designs of functional groups as junctions, various species, especially Au, can associate with the junction in a chiral fashion. [21–23] The chiroptics of helically arranged Au NPs have attracted intensive attention due to their novel optical activities, such as localized surface plasmon resonance (LSPR). [22,24–26] Combining chiral structures with metallic materials can create chiral plasmonic nanostructures to function as chiroptics over a broad spectral range depending on their structural dimensions, which is promising for the applications such as circular polarizers, chiroptical sensors, and negative refraction materials. [27–30] The chiral arrangement can create a chiral electromagnetic field to absorb or scatter circularly polarized light through inter-particle coupling selectively. Many groups fabricated helically arranged Au NPs in both solution and solid states, [22,31–35] and some simulation results also show the highly tunable chiroptic spectra. [33,36] However, most systems used structures from solution-state fabrication, resulting in limited applications in devices. A scalable method for the fabrication of solid chiroptical devices thus needs to be developed.

This work aims to demonstrate the fabrication of polymeric thin films with helically deployed Au NPs with CD signals of LSPR from the helical Au NP arrays with preferred handedness. Enantiomeric PS-PLLA and PS-PDLA with disulfide junctions (PS-ss-PLLA and PS-ss-PDLA) are synthesized (Fig. 1A). By taking advantage of induced chirality for those disulfide junctions, those junctions preferentially arranged in a one-handed helical array at the microphase-separated interface of the BCP* with helical phase from self-assembly can be formed. After hydrolysis of polylactide in the self-assembled BCP, those disulfide junctions can be successfully reduced into thiol (Fig. 1B), giving nanoporous PS with thiol-decorated nanochannels on the vitrified PS surface as a chiral template for association of reduced gold from electroless plating. After reducing Au ions, Au NPs arranged in a helical contour with specific handedness can be fabricated (Fig. 1C), creating a monolith with unique optical properties as chiral plasmonic metamaterials.

2 Experimental section

2.1 Synthesis of PS-ss-PLLA and PS-ss-PDLA

PS-*b*-PLLA BCP* with disulfide junction is denoted as PS-ss-PLLA. The PS-ss-PLLA and PS-ss-PDLA chiral block copolymers

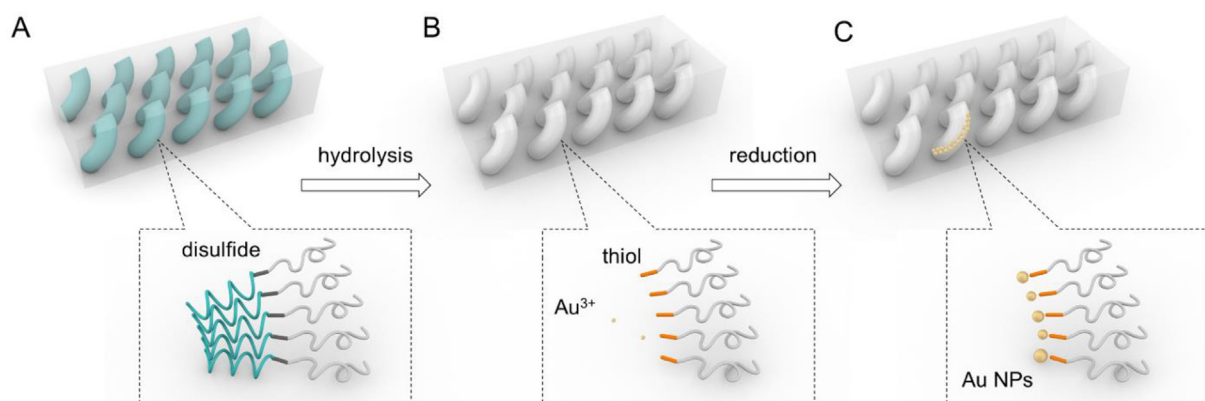
(BCPs*) were prepared by two-step polymerization (Fig. S1) using a new disulfide-labeled double-head initiator with hydroxyl (-OH) and Bromo (-Br) groups terminal (HO-ss-iBuBr) in either side that the Bromo group can process ATRP for styrene while the hydroxyl group inspires ROP for L-lactide. A disulfide-labeled double-head initiator was synthesized by adding Br-iBuBr dropwise to the mixed solvent containing 2-Hydroxyethyl disulfide and trimethylamine (Et₃N) in THF with stirring for 16 hours. The solid-state side products were then removed by vacuum filtration while the filtrates were concentrated by rotary evaporation and then washed with aqueous acidic and basic solutions three times. The residue was extracted with ethyl acetate (50 mL) and then dried with anhydrous Na₂SO₄. The product was purified by silica column chromatography with a mixture of ethyl acetate/hexane (3/7 v/v). The yellow oily product was obtained after the evaporation of solvents and further dried in a vacuum oven at room temperature overnight. The synthesis of a lactide-containing chiral block copolymer with thiol junction (*i.e.*, PS-ss-PLLA and PS-ss-PDLA) starts with ATRP for styrene using HO-ss-iBuBr/CuBr/HMTETA as the initiator/catalyst/ligand to give PS-ss-OH, followed with the ROP polymerization for L-lactide or D-lactide, using PS-ss-OH as macroinitiator. For the synthesis of PS-ss-PLLA and PS-ss-PDLA, the mixture of PS-ss-OH, L-lactide, and D-lactide using stannous octoate as a catalyst was introduced into a dry glass flask equipped with a magnetic stirrer in glovebox followed by reaction at 110°C for several hours. Consequently, PS-ss-PLLA and PS-ss-PDLA could be successfully obtained by the suggested synthetic routes, and the obtained products were quenched by ice followed by dissolution in CH₂Cl₂ with promoted precipitation in cold methanol. After drying in the oven for one day, the PS-ss-PLLA and PS-ss-PDLA block copolymers synthesized were further purified by acetonitrile for fractionation to remove undesired PLLA homopolymer and residual PS-ss-OH. After the fractionation, PS-ss-PLLA and PS-ss-PDLA with narrow molecular weight distribution would be expected.

2.2 Sample preparation

Bulk samples of PS-ss-PLLA and PS-ss-PDLA BCPs* were prepared by solution casting from dichloromethane (CH₂Cl₂) at room temperature (10 wt%). Samples were first dissolved in CH₂Cl₂ and filtrated through a syringe filter with a 0.45 μm pore size to remove the impurities. The solution was then transferred into a vial and sealed with aluminum foil. Furthermore, holes were punched into the aluminum foil using needles to allow solvent evaporation. The rate of evaporation was controlled by adjusting the number of holes. Bulk samples can be obtained after total solvent evaporation and further dried in a vacuum system to ensure the residual solvent. In addition, to eliminate the PLLA crystalline that might be formed during solution casting, samples were thermally treated at 180 °C for 5 minutes in a nitrogen atmosphere and then quenched at a rate of 150 °C/min to room temperature.

2.3 Hydrolysis and functionalization of template

The ordered samples were immersed in 1M sodium hydroxide (NaOH) for three days to remove the PLLA and washed with methanol. The samples can be obtained after drying

**Fig. 1**

Schematic illustration of fabricating polymeric thin films with helically deployed Au nanoparticles (Au NPs) using self-assembled chiral block copolymers (BCPs*) with controlled helicity as templates for reducing Au ions. (A) Disulfide junctions aligned in a helical fashion at the microphase-separated interface of the BCPs* with helical phase from the self-assembly of PS-ss-PLLA/PDLA; (B) After hydrolysis of polylactide in the PS-ss-PLLA/PDLA, disulfide groups can be reduced into thiol groups as association sites for Au ions; (C) Au NPs arranged in a helical contour with specific handedness can be formed after reduction of associated Au ions on the thiol junctions using hydrazine as a reducing agent.

in a vacuum system to ensure the removal of the residual solvent. After hydrolysis of PLLA, the sample was immersed in triphenylphosphine (PPh_3) mixed with ethanol for three days to reduce the disulfide junction to the thiol end group and then washed with ethanol. The PS template with the thiol end group can be obtained after drying in a vacuum to ensure residual solvent removal.

2.4 Reduction of Au NPs

For the nucleation process of Au NPs, the PS nanoporous template is first soaked into a low-concentration HAuCl_4 solution mixed with methanol. Note that methanol is used to enhance the wetting tendency of the precursor solution into the PS template through capillary force. Afterward, the porous template with the nanopores filled with Au ion aqueous solution was immersed into a mixed aqueous solution of methanol and hydrazinium hydroxide ($\text{N}_2\text{H}_5\text{OH}$) at room temperature for 6 hours. Immediately, the nucleation of Au seeds from reduction can be initialized at which Au ions can be reduced to Au nuclei by $\text{N}_2\text{H}_5\text{OH}$.

2.5 Characterizations

2.5.1 Transmission electron microscopy

Bright-field transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2100 LaB6 transmission electron microscope (at an accelerating voltage of 200 kV). Images were recorded on a Gatan CCD camera. The bulk samples of PS-ss-PLLA, PS-ss-PDLA and PS/Au were sectioned at room temperature by Leica Ultra-microtome with a thickness of 100nm. Afterward, the microsections were collected on copper grids (100 mesh). For neat polymer samples, PS was stained by RuO_4 to create the contrast from PLLA or PDLA. Staining is unnecessary for PS/Au since Au's electron density is large enough compared to PS to give a significant mass-thickness contrast.

2.5.2 Measurements of electronic CD, vibrational CD, LD and UV-Vis spectra

The film samples were positioned on quartz for the measurements. Electronic CD (ECD), LD and UV-Visible spectra were performed using a JASCO J-815 spectrometer at room temperature. Vibrational CD (VCD) spectra were performed using a JASCO FVS-6000 spectrometer at 4 °C. Scanning parameters were set as scanning speed, 200 °Cnm/min; digital integration time, 1s; twenty accumulations; data pitch, 0.1 nm; and bandwidth, 1 nm. The anisotropy g factor was calculated according to the following equation: $g = \frac{\text{CD}}{29980 \times \text{abs}}$, where abs is the absorption.

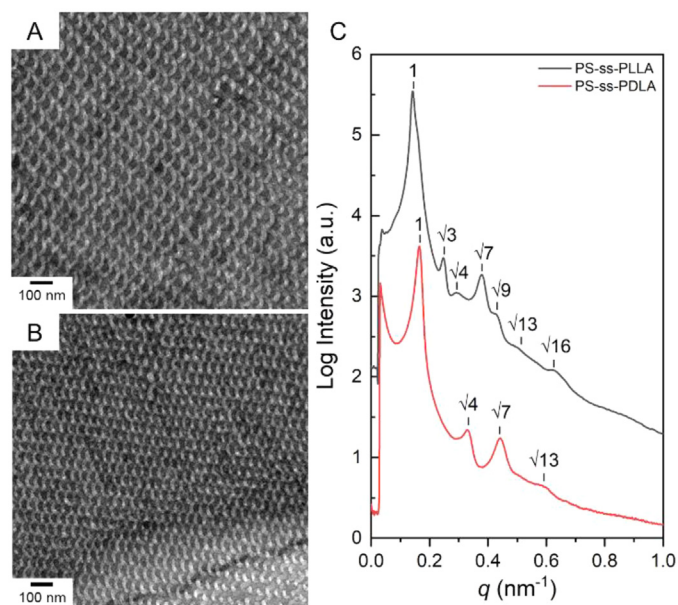
2.6 Simulation of optical extinction and corresponding CD spectrum

The optical simulation was performed by a 3D electromagnetic solver (FDTD Solutions, Lumerical Inc.).¹ The helically deployed Au NPs structure was constructed by Au NPs with a diameter of 3.5 nm randomly distributed in a helical shape with the helix radius of 20 nm, pitch length of 220 nm, and helical diameter of 50 nm. The optical extinction was calculated by the summation of absorption and scattering cross-sections. CD signals were obtained by the difference between extinctions of two circular polarization states. The refractive index of PS was 1.6. The dispersion of Au was the Lorenz-Drude model.

3 Results and discussion

3.1 Characterize of chiral diblock copolymer with functional junction

PS-ss-PLLA ($M_{n,\text{PS}} = 32,000$ g/mol, $M_{n,\text{PLLA}} = 17,000$ g/mol, $D = 1.28$, $f_{\text{PLLA}}^v = 0.3$) and PS-ss-PDLA ($M_{n,\text{PS}} = 28,000$ g/mol, $M_{n,\text{PDLA}} = 18,100$ g/mol, $D = 1.30$, $f_{\text{PDLA}}^v = 0.35$) were synthesized for self-assembly through solution casting in dichloromethane (CH_2Cl_2) at a concentration of 10 wt% (see *Supporting Information* for details). The solvent evaporation for casting was carried out for approximately five days, followed by thermal annealing at 180 °C for 5 minutes to annihilate the residual crystalline

**Fig. 2**

TEM micrographs of self-assembled (A) PS-ss-PLLA and (B) PS-ss-PDLA. (C) Corresponding one-dimensional SAXS profiles with characteristic reflections of a hexagonally packed helical phase of PS-ss-PLLA (black) and PS-ss-PDLA (red), respectively. PLLA and PS-ss-PDLA.

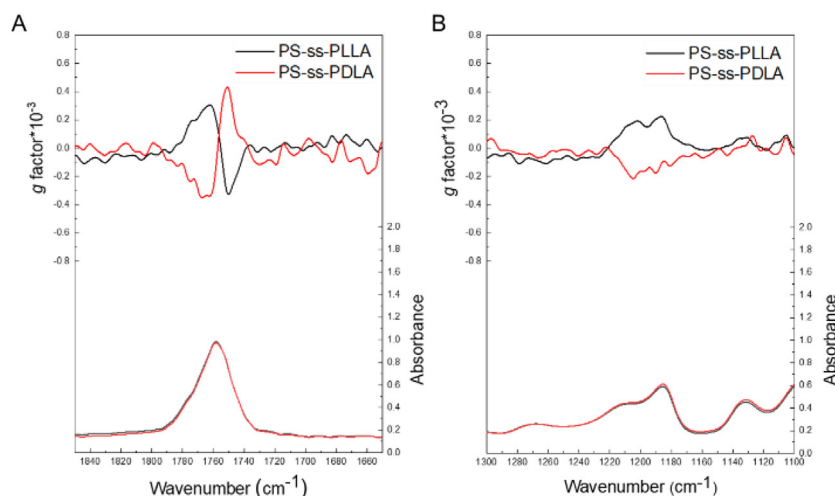
and then quenched to room temperature for characterization. Fig. 2A shows the TEM micrograph of the PS-ss-PLLA presenting polylactide microdomains with bright helical contours in the dark PS matrix after staining by RuO₄. Similar patterns can be observed in the PS-ss-PDLA (Fig. 2B). To further examine the forming morphologies from self-assembly, SAXS experiments were performed. As shown in the characteristic one-dimensional SAXS profiles (Fig. 2C), the reflections of PS-ss-PLLA and PS-ss-PDLA can be observed at the relative q values of 1: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$: $\sqrt{9}$: $\sqrt{13}$: $\sqrt{16}$ and 1: $\sqrt{4}$: $\sqrt{7}$: $\sqrt{13}$, respectively, further confirming the formation of a hexagonally-packed helix phase (H^* phase) with high degree of ordering. The lattice constant ($a = 2\pi/q$) of the hexagonally packed helices in self-assembled PS-ss-PLLA and PS-ss-PDLA are 44.5 and 37.9 nm, respectively. A simple estimation of the radius (r) of helices in hexagonally-packed arrays can be calculated according to the volume fraction ($f_{PL/DLA}^v$) and the lattice constant (a) of self-assembled BCPs: $r = \sqrt{\frac{\sqrt{3}a^2 f_{PL/DLA}^v}{2\pi}}$. [37] The radii of forming helices in self-assembled PS-ss-PL/DLA are approximately 12.8 and 11.8 nm. Moreover, by taking advantage of the homochiral evolution from the chiral monomers in chiral BCPs, a left-handed H^* phase can be obtained after self-assembly of PS-ss-PLLA; in contrast, a right-handed H^* phase forms in self-assembled PS-ss-PDLA. [14,37] To fabricate the nanostructured PS monolith with controlled handedness, BCP films were prepared by solution casting on the silica wafer to give the aimed monolithic helical phase. The vibrational circular dichroism (VCD) experiments for two monoliths with ordered texture were carried out to examine the handedness of the helical conformation of PS-ss-PL/DLA. A mirror image with split-type Cotton effects can be identified at 1755 cm⁻¹ in the VCD

spectra (Fig. 3A), which can be assigned to the C=O stretching in the carbonyl groups on the polylactide chain, suggesting that the polylactide chains indeed possess helical conformation with preferred handedness during self-assembly. These results are similar to the ones without the disulfide junction, [10,12,13] suggesting that the addition of the junction will not change the conformation of polylactide chains. More interestingly, a mirror image at the wavenumber within 1300 cm⁻¹ to 1100 cm⁻¹ in the VCD spectra can be identified in the solid-state BCP* films (Fig. 3B); these signals can be assigned to the absorption of the C-O-C vibrational mode on the polylactide main chain. Note that the C-O-C vibration mode is parallel to the main chain; the VCD signals thus suggest that the PLLA and PDLA chains are arranged helically due to inter-chain chiral interaction for packing with orientational order. Following the orientation of polylactide chains, the disulfide junction in the BCPs* should be helically arranged at the interface.

3.2 Helically arranged gold nanoparticles from templated synthesis

By taking advantage of the degradable ester group of chiral polylactide, it is feasible to create a template with helical nanochannels decorated with disulfide groups on the inner wall. The BCP* films were immersed in an aqueous sodium hydroxide (NaOH) solution for three days for selective etching of chiral polylactide microdomains to expose and reduce the disulfide groups into thiol groups to fabricate the nanostructured BCP template. The hydrolyzed samples were washed with a mixture of deionized water and methanol, followed by drying under a vacuum. Fig. S5 shows the Fourier transform infrared spectroscopy (FTIR) spectra before and after PS-ss-PLLA hydrolysis. The appearance of peaks at 1738 cm⁻¹ from C=O stretching and 1100 - 1300 cm⁻¹ from C-O-C stretching indicates the existence of a PLLA chain after polymerization. After the basic treatment, the FTIR spectra of hydrolyzed PS-ss-PLLA are similar to those from PS-ss-OH, confirming that the PLLA chains are successfully removed. Owing to the vitrified PS the disulfide junction retains the helical arrangement on the inner wall of the helical nanochannels after hydrolysis of the PLLA.

To associate Au ions on the helically arranged junctions, triphenylphosphine (Ph₃P) was used as a reduction agent to reduce disulfide groups into thiol end groups. The hydrolyzed samples were immersed in a mixture of Ph₃P with ethanol for three days at 40°C, followed by rinsing with ethanol. To further examine the nanostructured monolith after hydrolysis and end-group functionalization, the hydrolyzed and functionalized thin-film samples were observed by SEM. As shown in Fig. S7, the nanochannels can be clearly recognized with crescent-like texture and hexagonally packed pores resulting from hydrolyzed helices in the PS-ss-PLLA and PS-ss-PDLA films. Consequently, nanoporous PS monoliths with helical nanochannels can be successfully fabricated at which the thiol junctions with the helical arrangement can be decorated on the surface of the nanochannels as expected. The nanoporous PS with a thiol end group can serve as a template for the decoration of Au NPs in a helical deposition by reducing the Au ions in an aqueous solution. The PS nanoporous template was first immersed in

**Fig. 3**

VCD and corresponding FT-IR absorption spectra of (A) C=O and (B) C-O-C of PS-ss-PLLA (black) and PS-ss-PDLA (red) in the solid state.

a low-concentration HAuCl_4 solution mixed with methanol to introduce the Au ions in the nanochannels through capillary force. This step allows the Au ions to be absorbed on the sulfur site of the thiol group. Subsequently, the porous template with the nanopores filled with the aqueous solution of Au ions was immersed into a mixed aqueous solution of methanol and hydrazinium hydroxide ($\text{N}_2\text{H}_5\text{OH}$) as a reducing agent at room temperature for six hours. As a result, the Au ions can be reduced to Au NPs by $\text{N}_2\text{H}_5\text{OH}$. The presence of thiol groups promotes the formation of gold-sulfur bonds, which anchor the Au NPs to the sulfur sites. As a result, the Au NPs would be decorated on the helical arrangement of the thiol groups.

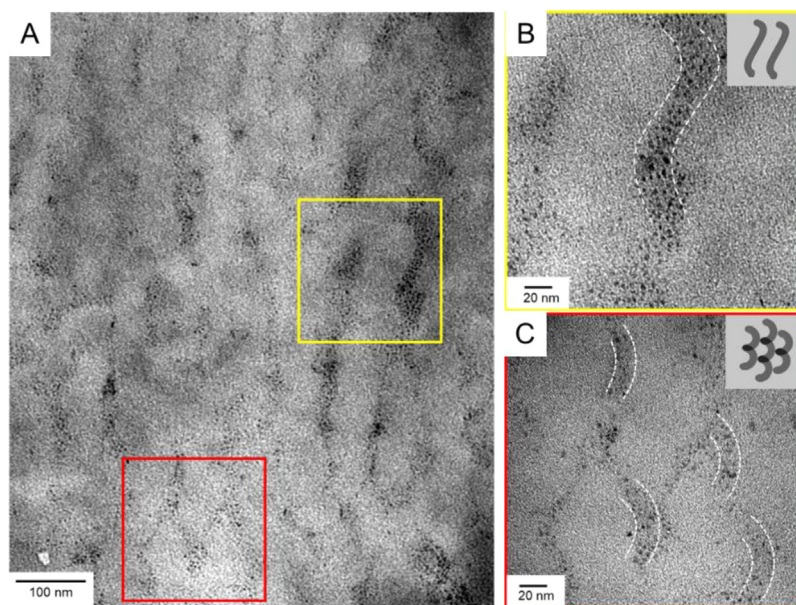
To evidence the formation of Au NPs in the PS nanochannels, the Au NP-decorated samples were observed under TEM. Fig. 4A shows the decoration of Au NPs on the inner wall of the PS helical nanochannels after the reduction of Au ions. With the decoration of the Au NPs, a crescent-like texture can be found (Fig. 4B), which is in line with one of the projections from the helical structure, as shown in the inset. Also, a helical texture with the forming Au NPs can be identified in a different projection (Fig. 4C), as illustrated in the inset. More images of the Au NP-decorated helical nanochannels are shown in Fig. S6. The diameter of the Au NPs is around 3.5 nm with a Gaussian distribution ranging from 2 nm to 5 nm based on the imaging results of over 200 NPs. Owing to the association of Au NPs with the thiol functional groups, the Au NPs could be controlled with a small size as found.

3.3 Experimental and simulation results of chiroptical properties

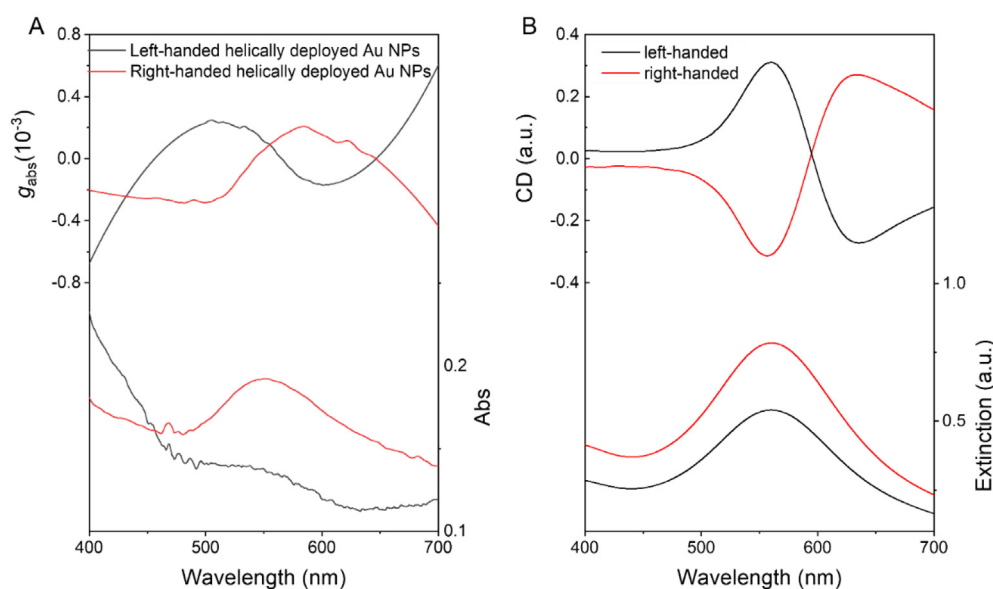
The films with left- or right-handed helically deployed Au NPs were examined by electronic circular dichroism (ECD) to characterize the chiroptical behaviors. Fig. 5 shows the ECD and UV-Vis spectra of the plasmonic film with left (black) and right-handed (red) helically deployed Au NPs on a quartz substrate. The absorption band in UV-Vis spectra centers at 550 nm, corresponding to the LSPR of Au NPs. The CD signal shows an up-and-down shape from long to short wavelength, exhibiting

a bisignate chiral response. When nonchiral NPs are arranged in a chiral geometry, chiral responses may be induced due to the interparticle plasmonic configuration. Similarly, the UV-Vis spectrum of the left-handed sample shows absorption at 550 nm but with a significant slope under 450 nm (black line in Fig. 5); the one at 550 nm can be assigned to the LSPR of Au NPs, and the slope under 450 nm might be attributed to the scattering from the template with the well-ordered hexagonally packed helices in line with the experimental results (SAXS). Compared to the right-handed sample, a bisignate CD signal with an opposite curve in the left-handed sample can be observed in the CD spectrum. As a result, a mirror image can be found in these two samples with different handedness. The mirror image indicates that the Au NPs in the two samples interact in similar helical arrangements but with opposite chirality, suggesting that the chiroptical properties indeed originated from the inter-particle coupling.

Optical simulations based on FDTD was carried out to examine the chiroptical properties of the helically deployed Au NPs. In the simulations, Au NPs with a diameter of 3.5 nm are randomly distributed in a helical geometry with a helix radius of 20 nm, pitch length of 220 nm, and helical diameter of 50 nm, in line with the observation of Au NPs under TEM (Fig. S6). The simulated optical properties of right-handed deployed Au NPs are shown in Fig. 5B. The optical extinction shows the same plasmonic band around 550 nm as observed in the experiment, ascribed to the resonance of the Au NPs. The ECD signal displays an evident bisignate behavior around the plasmonic resonance, also exhibiting an up-and-down shape from long to short wavelength as seen in the experiment. If Au NPs are deployed in the helical shape of opposite handedness, the bisignate ECD signal with an opposite curve can be obtained. Note that the experimental curve is the collective response of the film consisting of a broad distribution of helically deployed Au NPs with various sizes and orientations. The complex interactions of modes may result in profile changes and spectral shifts. As a result, the spectral profile exhibits some discrepancies compared to that of the

**Fig. 4**

TEM micrographs of (A) Au NPs deployed on the inner wall of the PS with helical nanochannels *via* templated reduction, giving the imaging of (B) and (C) with different projection angles. The insets show the helical structure viewing in different directions.

**Fig. 5**

(A) Experimental and (B) simulated CD and the corresponding UV-Vis spectra of left- (black) and right-handed (red) helically deployed Au NPs on the inner wall of the PS nanoporous template.

experiment. Even though the exact shapes and distributions of the helically deployed Au NPs within the measurement area are difficult to acquire, the characteristic chiroptical features of the helically deployed Au NPs can be revealed both experimentally and theoretically.

The reduction of Au NPs using PS-PLLA (without the disulfide group) for template fabrication was conducted to further examine the coupling effect. Fig. S8 shows the corresponding ECD and UV-Vis spectra, in which the absorption band centers at 530 nm.

Compared to the results in Fig. 5, there is a blue shift in the absorption band, which might be attributed to the disappearance of inter-particle coupling. Additionally, no significant CD can be observed in Fig. S8, indicating no chirality effect, further demonstrating that the existence of the thiol end group is critical in deploying Au NPs in a helical fashion.

Since the chiroptics originate from the inter-particle coupling of Au NPs, there should be no ECD signal over 650 nm in helically deployed Au NPs. However, the responsive curves obtained from

left- and right-handed samples diverge at the higher wavelength region in opposite direct ions. The reason could be either linear dichroism (LD), linear birefringence (LB), or scattering from the prepared monolith. Owing to the inherent anisotropy of the helical geometry, the electric dipoles of the helically deployed Au NPs might have preferred orientation in the film state, leading to LD and LB effects that would result in artificial ECD signals, especially in the solid state. LD and LB measurements were performed to clarify the origins of plasmonic ECD signals. Fig. S9 shows that the values of the corresponding LD from 400 to 700 nm are smaller than 0.005 in both samples, indicating that there should be no anisotropic effect on the spectroscopic measurements in the films. With the use of a gypsum plate for polarized light microscopy (PLM) observation, it is possible to justify the LB effect. As observed in the PLM images, both the left- and right-handed samples show a red-violet color. The color remains unchanged after rotating the sample by 90° (Fig. S10), indicating no LB effect. These results suggest that the ECD signals are truly contributed to the LSPR effect of helically deployed Au NPs. Therefore, we speculate that complicated coupling between multiple Au NPs might be the major contribution to the ECD signals above 650 nm in the spectra. Owing to the short distance between Au NPs, the NPs may interact with more than one NPs that might result in far-field coupling. Consequently, the CD signals may be more complicated than the case studied before with perfect helical arrangement. [36] As found, the left-handed one gives positive signals, and the other gives negative signals, showing high coherency to the handedness of the Au NPs arrangement.

4 Conclusions

In conclusion, polylactide-based BCPs* with disulfide junction (PS-ss-PLLA and PS-ss-PDLA) were synthesized for self-assembly to give the formation of H* phase. By taking advantage of the induced chirality of the disulfide junctions and the corresponding chirality memory effect, nanoporous PS with thiol junction from self-assembled PS-ss-PLLA and PS-ss-PDLA after hydrolysis and functionalization can serve as a chiral template for association with the reduced Au NPs. After reduction, Au NPs can be deployed on the inner wall of the PS nanoporous template. For the plasmonic behavior of helically deployed Au NPs, both the absorptions of left- and right-handed helically deployed Au NPs center at approximately 550 nm, which corresponds to the LSPR band. The bisignate ECD spectra originating from the plasmonic films with preferred handedness can be observed due to the dipole-dipole interaction between Au NPs. This strategy provides a scalable process for fabricating one-handed helical deployed Au NPs in polymeric films. By taking advantage of the optical properties of the well-arranged Au NPs array in the thin-film state further provides promising chiral plasmonic metamaterials in future applications as devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Hsiu-Wen Tsai: Writing – original draft, Investigation. **Sheng-Wei Shao:** Writing – review & editing, Visualization, Investigation. **Po-Ting Chiu:** Visualization, Investigation. **Cheng-Yen Chang:** Writing – review & editing, Investigation. **Yu-Chuan Sung:** Investigation. **Guan-Hong Li:** Formal analysis. **Yi-Ching Chen:** Formal analysis. **Akemi Kumagai:** Investigation. **Hiroshi Jinnai:** Conceptualization. **Yu-Chueh Hung:** Conceptualization. **Jing-Cherng Tsai:** Conceptualization. **Rong-Ming Ho:** Supervision, Funding acquisition, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.giant.2024.100350.

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