

Peer Review File

Spatiotemporally modulated full-polarized light emission for multiplexed optical encryption



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This paper fabricated a six-polarized-elemental-pixels-based device by integrating the spatiotemporal modulation from LED devices, the precise polarization control through nanomaterial self-assembly, and the programmable patterning and positioning facilitated by 3D printing. The device achieved an extremely high degree of polarization for both linearly and circularly polarized emission from ultrathin inorganic nanowires and quantum nanorods. It also demonstrated real-time polarization modulation covering the entire Poincaré sphere through the programming of the on-off state of each LED pixel. This innovative strategy offers a robust provides an excellent platform for multiplexing spatiotemporal polarization information, enhancing the security of visible light communication applications. The concept is new. Therefore, the reviewer believed this study is of interest for a broad audience, which could warrant publication in Nature Communications. However, a few details need to be addressed:

1. The alignment mechanism of nanorods during extrusion 3D printing should be clarified further. Specifically, how do the larger aspect ratio nanowires template the alignment of the nanorods? This is important for understanding the fundamentals behind achieving high degrees of polarization.
2. Please provide the layer number of the printed NWs film in the section of “Integration of the polarized LED device”.
3. In Fig. 2d, the printed films exhibited a substantial phase retardation across the visible wavelength range, increasing in proportion to the printing layer numbers. It would be meaningful to explore the change trend of luminous intensity with the increase of the printing layer numbers. Are there any noticeable decreases?
4. Long-distance visible light communication is significant. While the device exhibited lower bit error rate (BER) performance, it is important to clarify the signal transmission distance in discussions concerning secrecy rate and energy efficiency. How long is the effective signal transmission distance?
5. More characterization is needed on the stability and durability of the polarization performance over time, temperature, mechanical strain etc. This is critical for real applications.
6. There are numerous formatting issues in this paper that require attention and correction. For instance: the “lum” format in “glum” should be in subscript form; the “Fig.3E” should be changed to “Fig.3e” on page 8, line 26; In the references, the first letter of each word in the title should be consistently formatted.

Reviewer #2 (Remarks to the Author):

The manuscript introduces a approach in the realm of optical encryption by presenting a full-polarized light-emitting device that combines spatiotemporal modulation, nanomaterial assembly, and programmable 3D printing technologies. This integration facilitates encrypted displays characterized by

multiple polarization states, high gLUM values, exceptional energy efficiency, and the precise control of polarization states over time and space. The manuscript is organized well. However, there are certain critical aspects that need to be considered.

1. The manuscript discusses the dual role of ultrathin $\text{NiMoO}_4 \cdot x\text{H}_2\text{O}$ NWs in the development of a full-polarized light-emitting device for multiplexed optical encryption. On page 7, it is noted that these NWs act as a template for semiconductor NR alignment, which is a critical structural function. Concurrently, these NWs are also described as constituents of a novel birefringent ink, alongside SIS polymer, aimed at facilitating phase retardation necessary for converting LPL into CPL. This dual functionality of the NWs introduces a complex scenario where their structural role in NR alignment potentially intersects with their optical contribution to the device's birefringent properties. The distinction between these roles is vital, as it underpins the device's design rationale and its operational efficacy. The manuscript, however, does not explicitly delineate how these roles are separated or whether the NWs' structural function impacts their contribution to phase retardation or vice versa.
2. The manuscript highlights the perfect alignment of NRs alongside NWs, as evidenced by STEM images. This alignment is crucial for the proposed optical encryption device's functionality. However, the manuscript does not convincingly demonstrate the uniform distribution of NRs throughout the printed films. Such uniformity is critical for ensuring consistent photoluminescence intensity and DOP values across the device. A more thorough characterization, possibly incorporating additional imaging techniques or quantitative analyses, would be beneficial to confirm the dispersity of NRs in the printed films.
3. In Figure 3e, the normalized Stokes parameters exhibit a low signal-to-noise ratio after integrating the chiral plasmonic film into the device structure. Does this observed noise suggest an inherent limitation of the current design when it comes to managing signal integrity in the presence of these films? Addressing whether this noise indicates a fundamental limitation or can be mitigated through design adjustments would strengthen the manuscript.
4. The authors introduce the use of chiral plasmonic films, specifically assembled 432 helicoid III, to modulate the polarization states of emitted light, a critical aspect for the proposed optical encryption device. The CD and ORD spectra presented for these films provide initial insights into their chiral properties. However, the characterization appears incomplete without detailed information on key optical parameters such as the extinction property and the g-factor, both of which are essential for understanding the films' effectiveness as polarization modulators. Second, the authors chose high g-factor 432 helicoid III to further modulate the polarization states. Are chiral plasmonic films with low g-factor values or other chiral inorganic films also able to similarly serve as the polarization modulator? Are there certain requirements for the magnitude of the g-factor or the type of material to act as polarization modulator?
5. More importantly, the authors need to further elaborate the detailed modulation mechanism causing by chiral plasmonic films. Considering that chiral plasmonic nanoparticles typically exist as enantiomers with opposite handedness, the manuscript would benefit from a discussion on how films with different handedness influence the polarization states. Are the modulation effects of films with opposite chirality corresponding or opposite? A detailed exploration of the modulation mechanisms induced by chiral plasmonic films, would contribute significantly to the understanding of the device's functionality and its underlying principles.
6. The detailed operation conditions of the instruments and detailed optical materials parameters were not provided, makes it challenging for peers to replicate the study or to fully understand the basis of the

conclusions drawn. This is essential for scientific transparency and to enable other researchers to build upon this work effectively.

Response to Reviewers

We highly appreciate your careful review on our manuscript. We are especially thankful for your recognition of the novel concept we propose, which involves multiplexed optical encryption through multidimensional control of space, time, and polarization of light. All of your constructive comments helped to significantly improve our manuscript by performing further experiments and adding additional discussion. In the revised manuscript, we mainly 1) delve deeper into the properties and behaviors of the core materials (nanorods and nanowires) constituting our device, 2) comprehensively explore the polarization modulation aspects by various materials, especially in terms of chirality, and 3) validate the practicality of the device and the effectiveness of as-designed visible light communication system.

We are grateful to all the reviewers for their valuable comments, which certainly helped us improve the novelty and clarity of our manuscript. Our point-by-point responses to reviewers' comments are presented below. New texts added in the revised manuscript are indicated in yellow, and new texts in the supplementary information are indicated in blue. The figures that are only applicable to the response letter are indicated in green.

Reviewer #1

This paper fabricated a six-polarized-elemental-pixels-based device by integrating the spatiotemporal modulation from LED devices, the precise polarization control through nanomaterial self-assembly, and the programmable patterning and positioning facilitated by 3D printing. The device achieved an extremely high degree of polarization for both linearly and circularly polarized emission from ultrathin inorganic nanowires and quantum nanorods. It also demonstrated real-time polarization modulation covering the entire Poincaré sphere through the programming of the on-off state of each LED pixel. This innovative strategy offers a robust provides an excellent platform for multiplexing spatiotemporal polarization information, enhancing the security of visible light communication applications. The concept is new. Therefore, the reviewer believed this study is of interest for a broad audience, which could warrant publication in Nature Communications. However, a few details need to be addressed:

[Response]

We truly appreciate your valuable suggestions and comments. We particularly appreciate your acknowledgment of the major significance of our work; full-polarization control with a high degree of polarization and its application for spatiotemporally multiplexed optical communication. In accordance with your insightful comments, we have added detailed descriptions for the contents you suggested, aiming to convey information more clearly. Your comments certainly improved the manuscript, and the detailed point-by-point responses to your comments are as follows.

Specific Comments:

Comment 1. The alignment mechanism of nanorods during extrusion 3D printing should be clarified further. Specifically, how do the larger aspect ratio nanowires template the alignment of the nanorods? This is important for understanding the fundamentals behind achieving high degrees of polarization.

[Response]

We highly appreciate your thoughtful comments. During the direct ink writing process, shear forces are induced due to the flow of viscous ink through the nozzle. This shear force causes one-dimensional materials to align parallel with the shear force direction. In this case, nanowires are more easily aligned with their ultra-large aspect ratios and mechanical flexibility.

Nanorods with a much lower aspect ratio can also be aligned but with a much lower alignment degree, as revealed in our control experiment (Fig. S6). When nanowires and nanorods are mixed, nanowires act as the template to induce the good alignment of nanorods, resulting in a high degree of polarization. Fig. S4 demonstrates the STEM image of the ultramicrotomy section cutting vertically to the printing direction, which shows the distribution of nanorods and nanowires in the printed film. As can be seen, nanorods are surrounded by nanowires. The steric hindrance of the surrounding nanowires forces the nanorods to align parallel with the nanowires. As a result, the nanorods are perfectly aligned with a high degree of polarization.

To clarify the alignment mechanism, we revised our manuscript as below.

[Page 7 line 3 ~ line 7]

During DIW printing, shear forces are induced due to the flow of viscous ink through the nozzle, causing the embedded one-dimensional materials to align parallel with the shear force direction. In this case, nanowires are more easily aligned with their ultra-large aspect ratios and mechanical flexibility, which act as a template to align NRs parallel with the nanowires^{39,40} (Fig. 2b).

Comment 2. Please provide the layer number of the printed NWs film in the section of “Integration of the polarized LED device”.

[Response]

We appreciate your valuable comments. For the device integration, we printed 4 layers of NWs film on top of the aligned NR/NW film. These 4 layers of NWs offer the phase retardation to convert linearly polarized emission into circularly polarized light. We sought to convey accurate information to readers by precisely stating the relevant contents. The revised texts in the manuscript are included below.

[Page 25 line 21 ~ line 24]

For linear polarization pixels, 4 layers of aligned NW/NR films were printed with an interlayer distance of 30 μm . For the circular polarization pixels, 4 layers of birefringent NW films were printed on top of the linear polarization pixels, with an interlayer distance of 30 μm .

Comment 3. *In Fig. 2d, the printed films exhibited a substantial phase retardation across the visible wavelength range, increasing in proportion to the printing layer numbers. It would be meaningful to explore the change trend of luminous intensity with the increase of the printing layer numbers. Are there any noticeable decreases?*

[Response]

We thank you for your insightful comments. One of the reasons we choose $\text{NiMoO}_4 \cdot x\text{H}_2\text{O}$ nanowires for printing the phase retardation layer is their good transparency in the visible wavelength range from 500 nm to 650 nm, as shown in Fig. S3d. According to your comment, we explored the changing trend of luminous intensity with the increase of the printing layer numbers. The results show that the decrease in intensity is minimal even when we printed 4 layers of films for the phase retardance into circular polarization (Fig. R1). The added supplementary figure and statements are included below.

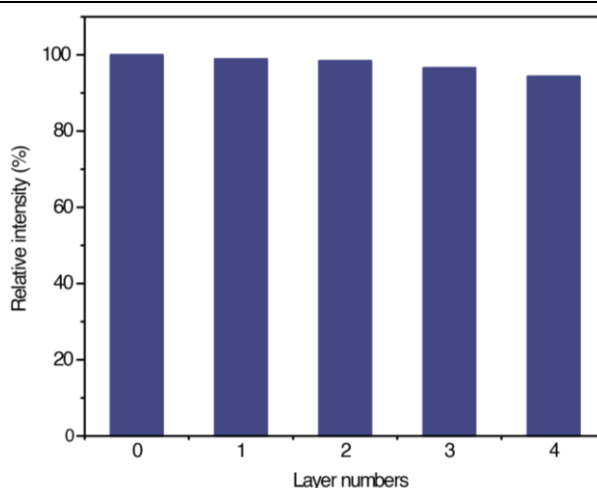


Figure R1 (Figure S10) | Luminous intensity depending on the number of NW layers.

[Page 7 line 34 ~ page 8 line 3]

Due to the transparency of NWs in the visible wavelength range from 500 nm to 650 nm, the NW layer does not decrease the luminous intensity of the NR film significantly (Fig. S10), maintaining high light efficiency.

Comment 4. Long-distance visible light communication is significant. While the device exhibited lower bit error rate (BER) performance, it is important to clarify the signal transmission distance in discussions concerning secrecy rate and energy efficiency. How long is the effective signal transmission distance?

[Response]

We truly appreciate your valuable comments. The achievable communication distance in visible light communication (VLC) system is important in general due to the strong path-loss for visible spectrum. In our manuscript, we have considered an indoor chiral plasmonics-enabled polarized VLC system having the distance between an LED and a photodiode (PD) of about 3 m. To evaluate the achievable communication distance specifically for a target bit error rate (BER), we first represent the union bound of BER for an arbitrary constellation set as [Ref1]:

$$\text{BER} \approx \frac{1}{M \log_2 M} \sum_{i=1}^M \sum_{j=1, j \neq i}^M d_H(\mathbf{x}_i, \mathbf{x}_j) Q\left(\frac{P_{\text{TX}}}{2\sigma} \|\mathbf{H}(\mathbf{x}_j - \mathbf{x}_i)\|\right) \quad (\text{R1})$$

where M is the modulation order for the arbitrary constellation set, $d_H(\mathbf{x}_i, \mathbf{x}_j)$ is the hamming distance between transmitted symbol vectors $\mathbf{x}_i$ and $\mathbf{x}_j$, and $Q(\cdot)$ is the Q function. The equation (R1) is a general representation for multiple-input and multiple-output (MIMO) systems. But in this response letter, we only consider a single-input and single-output (SISO) system to extract the distance between an LED and a PD from the proposed VLC channel. Please note that with MIMO systems, the achievable communication distance can be increased through advanced techniques including beamforming [Ref2]. The union bound of BER for M -ary pulse amplitude modulation (PAM) at the legitimate receiver (Bob) is obtained as:

$$\text{BER}_{\text{M-PAM}} \approx \frac{1}{M \log_2 M} \sum_{i=1}^M \sum_{j=1, j \neq i}^M d_{\text{H}}(x_i, x_j) Q\left(\frac{P_{\text{TX}}}{2\sigma_{\text{B}}} |h_{\text{B,d}} \cdot (x_j - x_i)|\right) \quad (\text{R2})$$

Thus, the BER for 4-ary PAM can be derived as:

$$\text{BER}_{4\text{-PAM}} \approx \frac{3}{4} Q(x) + Q(2x) + \frac{1}{4} Q(3x) \quad (\text{R3})$$

where $x = \frac{P_{\text{TX}}}{2\sigma_{\text{B}}} h_{\text{B,d}} d_{4\text{-PAM}}$ with the adjacent distance between 4-ary PAM symbols $d_{4\text{-PAM}}$, and the differential part of channels $h_{\text{B,d}}$:

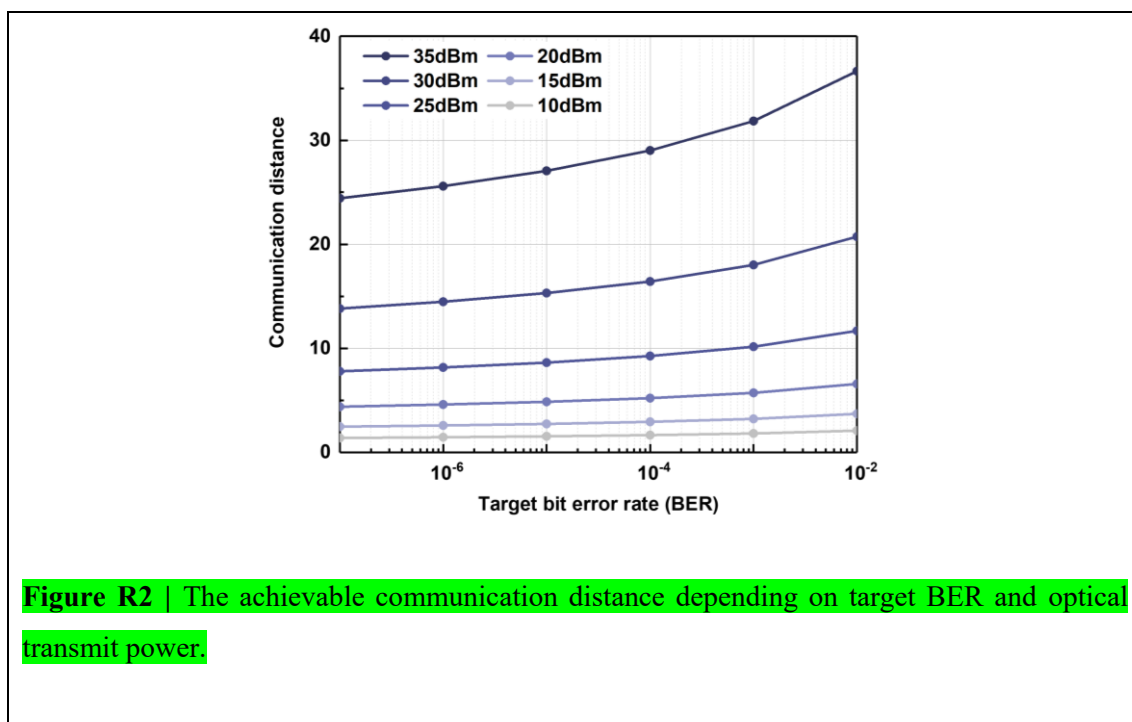
$$h_{\text{B,d}} = L_{\text{B}} \int_{\lambda^{\text{OF},\text{I}}(\theta_{\text{B}})}^{\lambda^{\text{OF},\text{U}}(\theta_{\text{B}})} \left(R^{\text{PD}}(\lambda) S^{\text{LED}}(\lambda) (\bar{a}_{\text{L}}(\lambda) - \bar{a}_{\text{R}}(\lambda)) \right) d\lambda = L_{\text{B}} \cdot \bar{h}_{\text{B,d}} \quad (\text{R4})$$

with $L_{\text{B}} = \frac{(m_{\text{LED}}+1)A_{\text{PD}}}{2\pi D_{\text{B}}^2} \cos^{m_{\text{LED}}} \psi_{\text{B}} \cos \theta_{\text{B}}$. We finally derive the achievable communication distance for a given BER_{PAM} using (R2) and (R3) as:

$$D_{\text{B}} \approx \sqrt{\frac{P_{\text{TX}}}{2\sigma_{\text{B}} \cdot \hat{x}} \cdot \frac{(m_{\text{LED}} + 1)A_{\text{PD}}}{2\pi} \cos^{m_{\text{LED}}} \psi_{\text{B}} \cos \theta_{\text{B}} \cdot \bar{h}_{\text{B,d}} \cdot d_{4\text{-PAM}}} \quad (\text{R5})$$

where $\hat{x}$ is the solution of (R3), which is obtained by using the approximation of Q function in [Ref3]. The achievable communication distance depending on a target BER and optical transmit power can be obtained as in Fig. R2.

In Fig. R2, even though the achievable communication distance in the indoor scenario may seem short for low optical power to satisfy a target BER, it is not a significant issue since the practical power of indoor LEDs is usually higher than 30 dBm [Ref4]. Thus, the communication range of proposed VLC system in indoor scenarios is sufficient to achieve low BER with the advantages for secrecy rate and energy efficiency. For outdoor VLC systems such as a vehicular VLC system, the power of LED is much higher than that in indoor VLC systems, and the concentrated radiation pattern would be employed to support longer communication distance. Therefore, the achievable communication distance can be much longer for outdoor VLC systems compared to that of indoor VLC systems [Ref5].



Comment 5. *More characterization is needed on the stability and durability of the polarization performance over time, temperature, mechanical strain etc. This is critical for real applications.*

[Response]

We appreciate your valuable comments. We agree that the stability and durability of polarization performance are critical for real applications. Accordingly, we re-measured the polarization states of the integrated device fabricated 18 months ago (Fig. R3). The polarization states are well preserved compared with those measured 18 months ago, indicating robust stability. We anticipate such stability can be attributed to the intrinsic stability of inorganic NWs and the core-shell CdSe@CdS NRs. Besides, the polymer matrix can insulate oxygen and humidity, further enhancing the stability.

To investigate the temperature stability, we characterized the polarization and luminescence performance of the printed film at different temperatures using a polarization camera. Experiments show that the polarization direction remained even when the temperature of the substrate was raised to 150 °C for 10 minutes (Fig. R4). At the same time, the luminous intensity does not exhibit notable degradation at temperature as high as 100 °C. Such great stability over temperature is adequate for the color conversion layer of practical LED devices.

Furthermore, we note that the placement of the color conversion layer at the outermost layer of the device structure facilitates easy dissipation of thermal stress generated internally. Hence, this aspect is deemed non-critical to the issue at hand. Further, since the polarization films were printed on ultrathin glasses which are rigid, the mechanical strain will not affect the polarization performance at the device level.

Taking these, we have added figures and have revised texts in the manuscript and supplementary information document as included below.

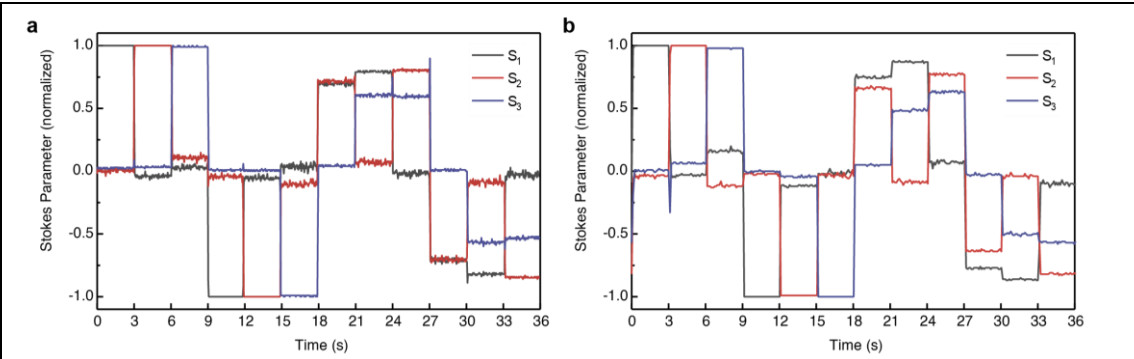


Figure R3 (Figure S12) | Polarization states of the integrated polarized LED devices well preserved over time. a, b, Normalized Stokes parameter measured at 27/10/2022 (a), and at 15/04/2024 (b).

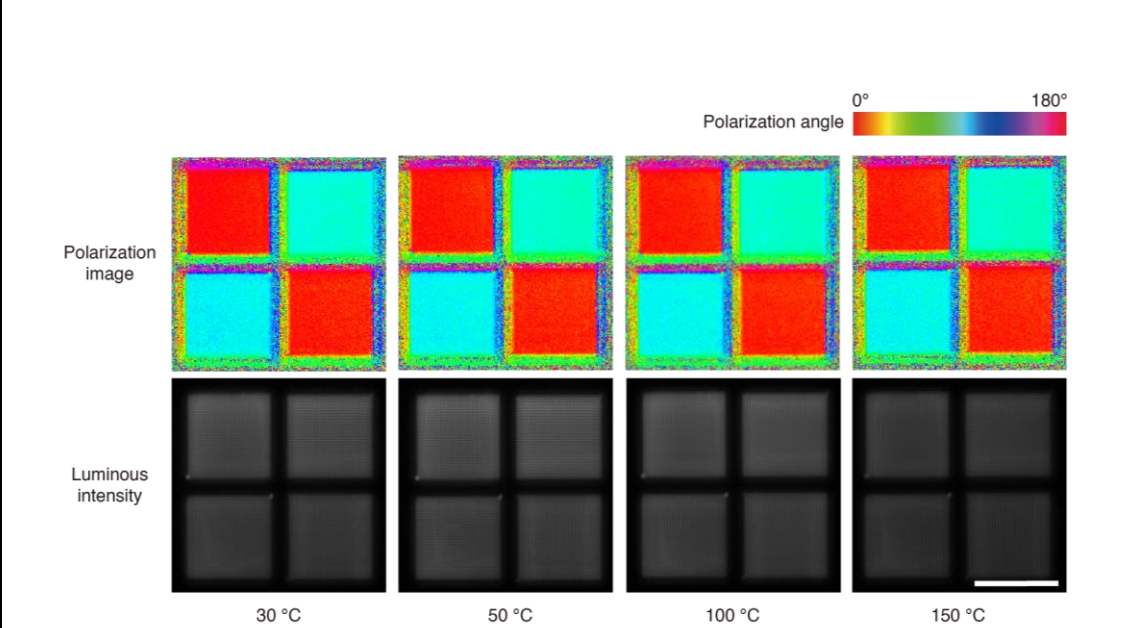


Figure R4 (Figure S13) | Polarization and luminescence performance of linearly polarized LED devices at different temperatures.

luminescent samples after heat treatment for 10 minutes on the hotplate at different temperatures. Scale bar, 1 cm.

[Page 8 line 8 ~ line 11]

The high DOP and glum value promise an efficient color conversion layer capable of transforming an ordinary micro-LED display panel into an effective and practical polarization controlling device alongside the validation of temporal and thermal stability (Fig. S12 and Fig. S13).

Comment 6. *There are numerous formatting issues in this paper that require attention and correction. For instance: the “lum” format in “glum” should be in subscript form; the “Fig.3E” should be changed to “Fig.3e” on page 8, line 26; In the references, the first letter of each word in the title should be consistently formatted.*

[Response]

We sincerely apologize for our mistakes. We have corrected the errors in our revised manuscript, including those you pointed out, and also checked if any parts of the manuscript contained miswritten content. Thanks for your effort to improve the quality of our manuscript.

You can find the list of corrections we made in the “List of Changes” section on the last page of this document.

Reviewer #2

The manuscript introduces a approach in the realm of optical encryption by presenting a full-polarized light-emitting device that combines spatiotemporal modulation, nanomaterial assembly, and programmable 3D printing technologies. This integration facilitates encrypted displays characterized by multiple polarization states, high glum values, exceptional energy efficiency, and the precise control of polarization states over time and space. The manuscript is organized well. However, there are certain critical aspects that need to be considered.

[Response]

We sincerely appreciate your efforts and time in reviewing our manuscript. Your perspective on this work assuredly improved the quality of our manuscript. In order to strengthen the significance of our work and address your concerns, we carried out additional measurements and enriched the discussion part. Essentially, we reexamined the contributions and behaviors of composing materials at multiple scales and added a comprehensive and diverse discussion on polarization control by polarization modulators.

You can find the detailed responses to your comments and the revised contents below.

Specific Comments:

Comment 1. The manuscript discusses the dual role of ultrathin NiMoO₄·xH₂O NWs in the development of a full-polarized light-emitting device for multiplexed optical encryption. On page 7, it is noted that these NWs act as a template for semiconductor NR alignment, which is a critical structural function. Concurrently, these NWs are also described as constituents of a novel birefringent ink, alongside SIS polymer, aimed at facilitating phase retardation necessary for converting LPL into CPL. This dual functionality of the NWs introduces a complex scenario where their structural role in NR alignment potentially intersects with their optical contribution to the device's birefringent properties. The distinction between these roles is vital, as it underpins the device's design rationale and its operational efficacy. The manuscript, however, does not explicitly delineate how these roles are separated or whether the NWs' structural function impacts their contribution to phase retardation or vice versa.

[Response]

We thank you for your valuable comments. In our design and the 3D printing process, the structural role in NR alignment and the phase retardation role of the NWs are separated. To print a linearly polarized emission NR layer, as shown in Fig. 2b, $\text{NiMoO}_4 \cdot x\text{H}_2\text{O}$ NWs act as a template to induce the alignment of NRs to emit linearly polarized light. Although NWs also result in phase retardation in this layer, the optical anisotropy axis of the birefringent layer is parallel with the NRs alignment and the LPL plane. As a result, the LPL is not affected by the phase retardation in this layer. So, we can conclude that in the LPL layer, NWs only manifest the structural role.

On the other hand, to get circularly polarized emission, NWs layers are printed on top of the NRs layer with a relative angle of -45 or $+45$ degrees. Due to the relative angle between the LPL plane and the optical anisotropy axis of the birefringent layer, the phase retardation of the NW layer manifest and convert LPL into CPL.

To explicitly show the separate roles of NWs in the structural template and phase retardation, we added sentences to the manuscript as below.

[Page 8 line 3 ~ line 5]

It should be noted, although a phase retardation is also present due to the NWs in the NR film layer, it does not affect the LPL because the optical anisotropy axis is parallel with the LPL polarization plane.

Comment 2. *The manuscript highlights the perfect alignment of NRs alongside NWs, as evidenced by STEM images. This alignment is crucial for the proposed optical encryption device's functionality. However, the manuscript does not convincingly demonstrate the uniform distribution of NRs throughout the printed films. Such uniformity is critical for ensuring consistent photoluminescence intensity and DOP values across the device. A more thorough characterization, possibly incorporating additional imaging techniques or quantitative analyses, would be beneficial to confirm the dispersity of NRs in the printed films.*

[Response]

We greatly appreciate your comments. As you pointed out, in terms of practical usage, uniform distribution and following consistent photoluminescence of consistently aligned NRs over nano and microscale is certainly important. In order to demonstrate the uniform

distribution of NRs at and beyond the microscale, we have included photographs captured with an optical camera and images obtained through confocal microscopy in Fig. R5. These images reveal consistent photoluminescence intensity spatially across the film spanning tens to thousands of micrometers. Considering that the pixel size of a typical PC monitor with Full HD resolution is approximately 300 μm , we can assert that the distribution of nanorods exhibits a high level of uniformity, which is sufficient for practical utilization without any significant deficiencies. Additionally, as evident from the image in Fig. S2f, high consistency is also observed for the polarization states across the area and samples.

We have added the images in supplementary information and revised the manuscript to highlight the uniformity of emission at various scales.

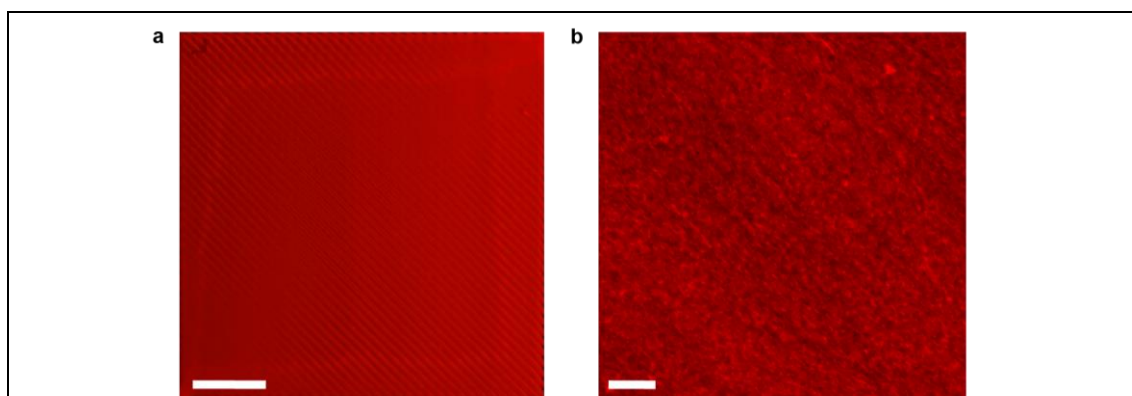


Figure R5 (Figure S5) | a, b, Photograph (a) and confocal microscopy (b) images of printed film showing great alignment of NRs in microscale. Scale bars, 2 mm (a) and 20 μm (b).

[Page 7 line 7 ~ line 9]

Microtome scanning transmission electron microscopy (STEM) and confocal microscopy images demonstrated the perfect alignment of NRs alongside NWs across nano and micro scales (Fig. 2c, Fig. S4, and Fig. S5).

Comment 3 & 4. *In Figure 3e, the normalized Stokes parameters exhibit a low signal-to-noise ratio after integrating the chiral plasmonic film into the device structure. Does this observed noise suggest an inherent limitation of the current design when it comes to managing*

signal integrity in the presence of these films? Addressing whether this noise indicates a fundamental limitation or can be mitigated through design adjustments would strengthen the manuscript.

The authors introduce the use of chiral plasmonic films, specifically assembled 432 helicoid III, to modulate the polarization states of emitted light, a critical aspect for the proposed optical encryption device. The CD and ORD spectra presented for these films provide initial insights into their chiral properties. However, the characterization appears incomplete without detailed information on key optical parameters such as the extinction property and the g-factor, both of which are essential for understanding the films' effectiveness as polarization modulators. Second, the authors chose high g-factor 432 helicoid III to further modulate the polarization states. Are chiral plasmonic films with low g-factor values or other chiral inorganic films also able to similarly serve as the polarization modulator? are there certain requirements for the magnitude of the g-factor or the type of material to as polarization modulator?

[Response]

We deeply appreciate for your valuable comments on our manuscript to enhance the novelty and advantages further. Given that your comments 3 and 4 are in the similar context for us to answer, we carefully address them together.

First of all, we fully agree with your comment that the modulation of polarization states is comprehensively determined by the optical properties of the polarization modulator, including extinction and g-value. In order to address your comment and provide clearer information for readers, we added the g-value and extinction spectra of the 432 helicoid III particles in Fig. 3c-e (Fig. R6). As evident from the spectra, a great loss of light intensity occurs at the wavelength of our point of interest, 650 nm, due to the localized surface plasmon resonance (LSPR) characteristics. The signal-to-noise ratio of the normalized Stokes parameter is determined by the intensity of the incident light on the photodiode within the polarimeter, hence revealing lower values when transmitted through plasmonic film. In particular, this phenomenon is more dominating for the polarization state ③ in Fig. 3e corresponding to RCP, since the particles have a negative circular dichroism value, i.e., a larger extinction property for RCP than for LCP. Therefore, this issue could be simply addressed by employing a higher output LED as the excitation source to enhance the emission intensity or utilizing detection equipment capable of integrating more light temporally or spatially compared to a polarimeter.

Alternatively, from the perspective of device design (material selection), there is the option of using materials with lower extinction. Compared to plasmonic materials, materials with considerably lower losses, such as assembled metal oxide nanowires (NiMoO_4)-based photonic crystals, can be utilized. For demonstration, we demonstrate the polarization modulation with previously reported chiral photonic crystal film of layer-by-layer assembled $\text{NiMoO}_4 \cdot x\text{H}_2\text{O}$ nanowires obtained by Langmuir–Schaefer technique [Ref6]. We illustrate the polarization modulation results based on this material in Fig. R7. This material, like 432 helicoid III in Fig 3, exhibits significant negative circular dichroism at 650 nm but with lower extinction, resulting in a higher g-value. Similar to the results in Fig 3e, the polarization state selectively changes to left-handed. The observed changes in S1 and S2 are relatively noticeable due to the relatively larger ORD values compared to 432 helicoid III. Furthermore, due to the significantly lower magnitude of extinction, a much higher signal-to-noise ratio is evident compared to the chiral plasmonic film. These results imply that the polarization modulator proposed in our device can be extended to various material groups with various optical properties, enhancing its applicability.

Meanwhile, the results of particles with low g-values intentionally restricted by reducing the amount of the chirality-inducing organic molecule (L-glutathione) [Ref7], we observe that the polarization state remains almost unchanged, thereby maintaining the emission state of the device nearly intact (Fig. R8). Though there is a slight variation in the signal-to-noise ratio, it is solely attributed to the extinction property of the particles. Given that the g-value represents the differential extinction for circular polarization relative to total extinction, a larger g-value implies a larger polarization control in the circular basis and thus indicates higher efficiency as a polarization modulator.

We added the above comprehensive descriptions and perspectives on the polarization modulation by various materials to the revised manuscript and supporting documents.

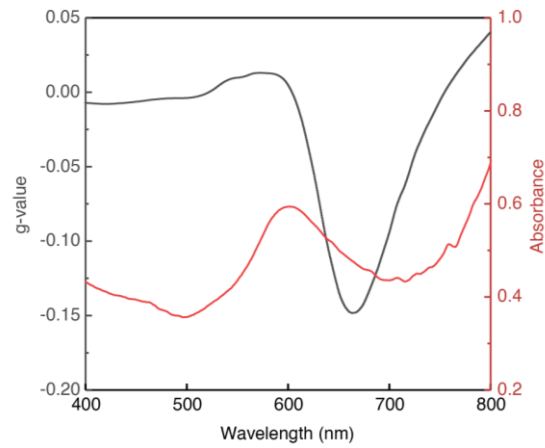


Figure R6 (Figure S17) | g-value and absorbance spectra of the chiral plasmonic film with assembled 432 helicoid III. The minimal g-value of the film was -0.148 at 663 nm.

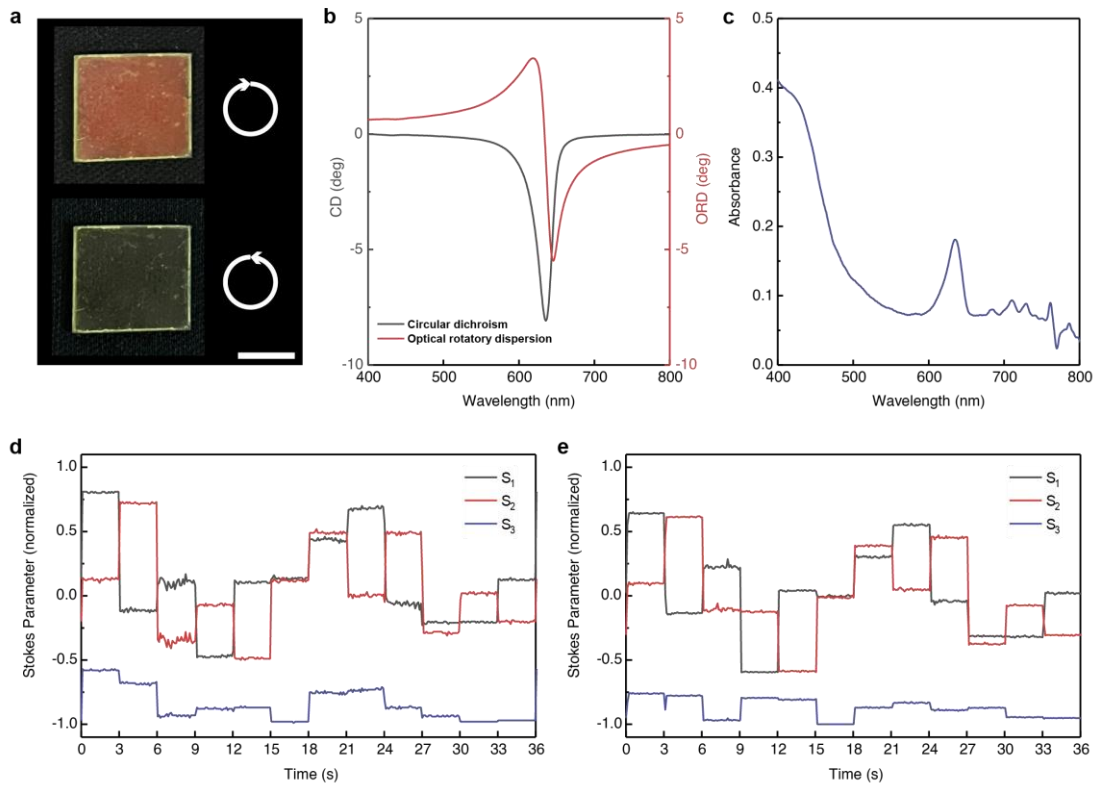


Figure R7 (Figure S19) | **a**, Photograph image of the chiral photonic crystal film viewed through circular polarizers. The film was obtained by layer-by-layer assembly of

NiMoO₄ · x H₂O nanowires⁷. **b, c**, CD and ORD (**b**) and absorbance (**c**) spectra of the chiral photonic crystal film. The minimal g-value of the film was -1.37 at 636 nm. **d, e**, Experimentally measured (**d**) and calculated (**e**) normalized Stokes parameters of the polarized light transmitted through the film. Scale bar, 5 mm (**a**).

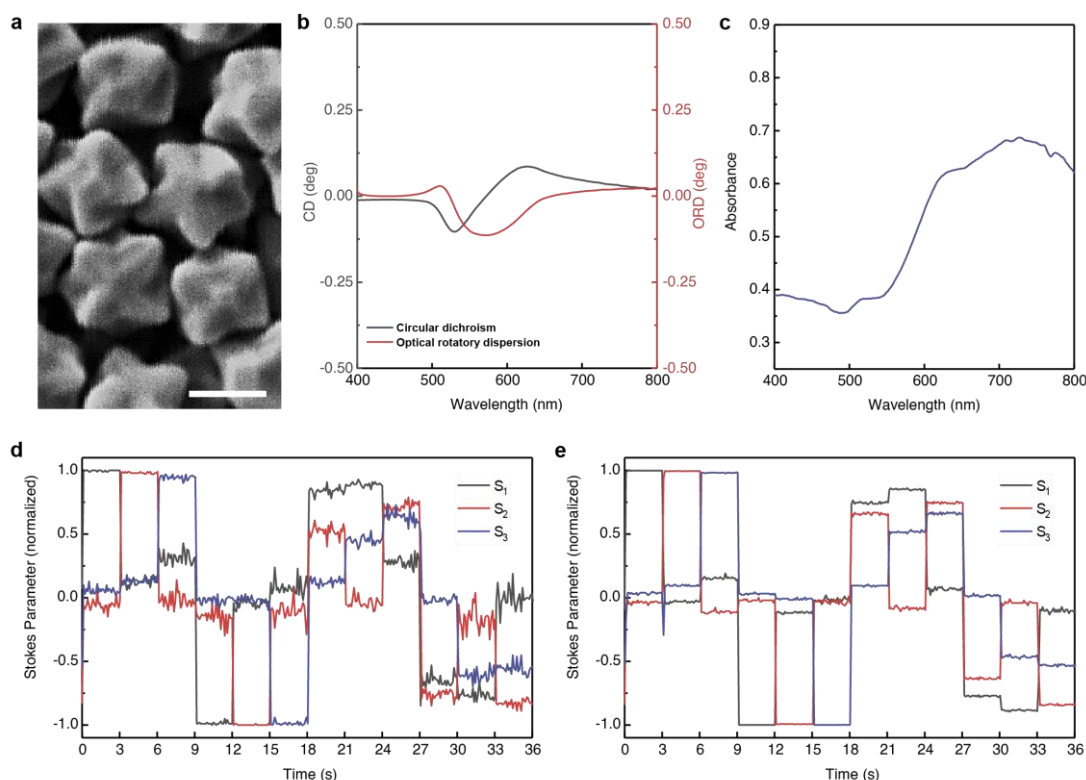


Figure R8 (Figure S20) | a, SEM image of the 432 helicoid III nanoparticles with low g-value. Stoichiometrically controlling the synthetic condition, the evolution of chiral motif was intentionally suppressed and thus the chiroptic response was induced to be weak. **b, c**, CD and ORD (**b**) and absorbance (**c**) spectra of the 432 helicoid III nanoparticle with low g-value. The maximal g-value of the particle was $+4.2 \times 10^{-3}$ at 625 nm. **d, e**, Experimentally measured (**d**) and calculated (**e**) normalized Stokes parameters of the polarized light transmitted through the particle. Scale bar, 100 nm (**a**). In contrast to the results shown in Fig. 3e, Fig. S18, and Fig. S19, it can be observed that polarization modulation scarcely occurs. In accordance with these results, we note that as the g-value of the polarization modulator (i.e., differential extinction for circular polarization relative to total extinction) increases, it performs its

polarization-controlling role more effectively.

[Page 8 line 33 ~ page 9 line 2]

Furthermore, the polarization states can be modulated by transmission through an ordered chiral plasmonic film consisting of 432 helicoid III (Fig. 3c), which exhibits strong CD responses in the visible wavelength range (Fig. 3d and Fig. S17)^{20,21}.

[Page 9 line 4 ~ line 13]

This modulation has been accurately accounted using the Muller matrix of the chiral plasmonic film derived from its CD and absorption spectra (Fig. S15c, d and Fig. S17). In addition, the utilization of chiral nanoparticles with opposite chirality could lead to the reversal of trajectories on the Poincaré sphere (Fig. S18), and the expandability of polarization modulators into various chiral inorganic materials has also been demonstrated (Fig. S19). Since the magnitude of this polarization modulation is determined by the relative effect of CD and extinction, that is, g-value, a chiral plasmonic film with a large g-value near -0.2 has superb modulation performance (Fig. 3d, e, and Fig. S20). Further, the broadly controllable optical properties of 432 helicoid III, tailored by their shape, size, composition, and assembly structure⁵¹, are expected to enhance the security of optical communication applications.

[Page 24 line 16 ~ line 18]

Suppression of the chirality evolution of nanoparticles was achieved by reducing H₂AuCl₄ and L-GSH to half in concentration (Fig. S20).

Comment 5. *More importantly, the authors need to further elaborate the detailed modulation mechanism causing by chiral plasmonic films. Considering that chiral plasmonic nanoparticles typically exist as enantiomers with opposite handedness, the manuscript would benefit from a discussion on how films with different handedness influence the polarization*

states. Are the modulation effects of films with opposite chirality corresponding or opposite? A detailed exploration of the modulation mechanisms induced by chiral plasmonic films, would contribute significantly to the understanding of the device's functionality and its underlying principles.

[Response]

We highly appreciate your insightful comments. The chiral nature of amino acids and peptides, coupled with stoichiometric control in nano-particle synthesis, enables the synthesis and modulation of chiral nanoparticles (432 helicoid III) with opposite chirality (i.e., the sign of circular dichroism). This serves as the foundation for achieving high controllability of the polarization state of the device. For instance, as you suggested, utilizing the enantiomeric peptide (D-glutathione), we demonstrated the polarization controlled by plasmonic nanoparticle with opposite chirality (Fig R9a to c, g-value of 0.16 at 650 nm). These particles, in contrast to the L-glutathione-directed particles in Fig. 3, absorbs more LCP than RCP and selectively transmit right-handed light, resulting in a positive S_3 as in Fig. R9d. Comparing the nanoparticle with opposite chirality, we depicted the trajectory of polarization modulation on the Poincaré sphere for six representative polarization states in Fig. R9e. Apart from the 12 pixel states implemented based on the state of the pixels, the selective polarization modulation of L and D particles is extendable to all possible polarization states. We have supported this with Mueller calculus-based calculation results depicted in Fig. R10, performed with the experimentally measured CD, ORD, and absorbance data. Such synthetic control over chirality can lead to interesting applications such as stereoscopic displays and optical cloaking by inducing a reversal in the circular basis of device emission. In accordance with your valuable suggestion, we have appended the polarization modulation results induced by nanoparticles with opposite chirality and the corresponding discussion as follows.

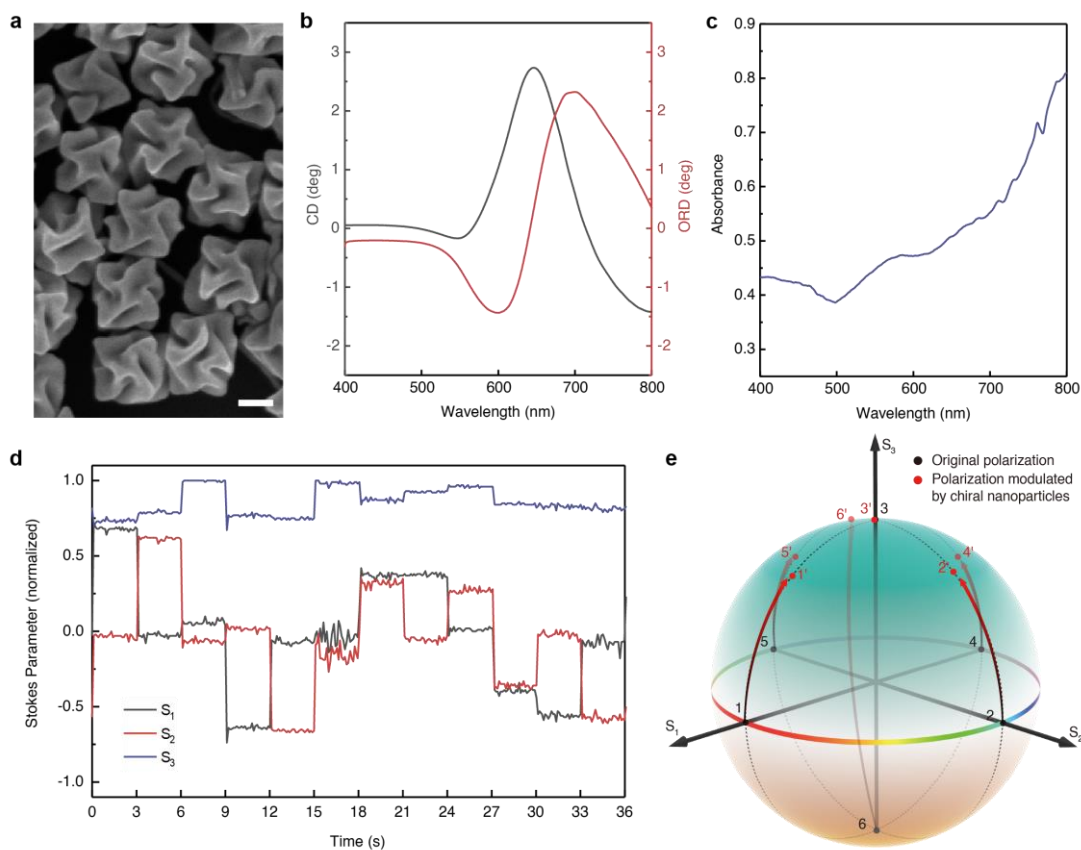


Figure R9 (Figure S18) | a, SEM image of the 432 helicoid III nanoparticles synthesized with D-glutathione (D-432 helicoid III). These particles have opposite chirality compared with those used in Fig. 3, Fig. S15, and Fig. S17 synthesized with L-glutathione (L-432 helicoid III). **b**, **c**, CD and ORD (**b**) and absorbance (**c**) spectra of the D-432 helicoid III. The g -value of the particles was +0.165 at 642.5 nm. **d**, Experimentally measured normalized Stokes parameters of the polarized light transmitted through the particles. **e**, Polarization modulation by D-432 helicoid III visualized on the polarization Poincaré sphere. Scale bar, 100 nm (**a**).

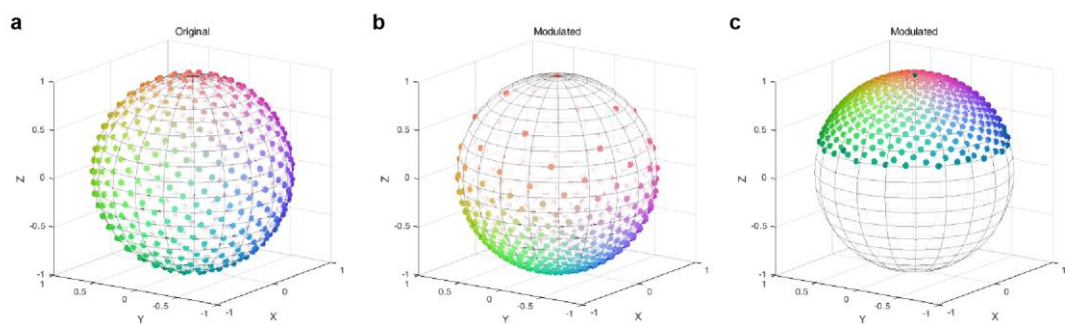


Figure R10 | Calculation results of polarization modulation by chiral nanoparticles of opposite chirality for 500 polarization states covering the surface of the polarization Poincaré sphere. **a**, Original polarization states. **b**, Polarization states modulated by L-432 helicoid III nanoparticles. **c**, Polarization states modulated by D-432 helicoid III nanoparticles.

[Page 9 line 6 ~ line 13]

In addition, the utilization of chiral nanoparticles with opposite chirality could lead to the reversal of trajectories on the Poincaré sphere (Fig. S18), and the expandability of polarization modulators into various chiral inorganic materials has also been demonstrated (Fig. S19). Since the magnitude of this polarization modulation is determined by the relative effect of CD and extinction, that is, g -value, a chiral plasmonic film with a large g -value near -0.2 has superb modulation performance (Fig. 3d, e, and Fig. S20). Further, the broadly controllable optical properties of 432 helicoid III, tailored by their shape, size, composition, and assembly structure⁵¹, are expected to enhance the security of optical communication applications.

[Page 24 line 11 ~ line 13]

The growth solution was prepared by adding 800 μL of 100 mM CTAB, 0.2 μL of 10 mM HAuCl_4 , 475 μL of 100 mM AA, and 5 μL of 5 mM L-GSH (or D-GSH) to 3.95 mL of deionized water.

Comment 6. The detailed operation conditions of the instruments and detailed optical materials parameters were not provided, makes it challenging for peers to replicate the study or to fully understand the basis of the conclusions drawn. This is essential for scientific transparency and to enable other researchers to build upon this work effectively.

[Response]

We thank you for your comment and apologize for a lack of clarity. We definitely agree with you and believe that providing a clearer description of our material and device will offer clarity to the multitude of scientists referencing our research, thus aiding the advancement of this field. We have minutely documented the optical properties (e.g., circular dichroism, optical rotatory dispersion, and absorbance) of various materials used in the experiments. We also have added a more detailed explanation to the Methods section in the revised manuscript as follows.

[Page 25 line 13 ~ line 26]

The 24 by 24 UV LED device operated under constant current. UV LED chips (CUN6LF1C) are purchased from Seoul Viosys company with the luminescence centered around 365 nm, and FWHM bandwidth of 10nm. A total of 576 UV-LEDs were equally spaced apart, arranged 24 by 24, and loaded onto a customized PCB to supply with the same current. The operation voltage was 3.3 V, and the forward current was 10 mA. To minimize interference between adjacent LEDs, the gaps between the LED cells were covered with 3D-printed barriers. To make the polarized LED device, we first print 24 by 24 polarized pixels on top of an ultrathin glass (Eagle-XG glass, Corning) with a thickness of 0.3 mm. Each pixel measures $3.5 \times 3.5 \text{ mm}^2$. Each 6 pixels form a unit, which contains 4 linear polarizations along 0, 45, 90 and 135 degrees and two opposite circular polarizations. For linear polarization pixels, 4 layers of aligned NW/NR films were printed with an interlayer distance of 30 μm . For the circular polarization pixels, 4 layers of birefringent NW films were printed on top of the linear polarization pixels, with an interlayer distance of 30 μm . Then, the printed pixels on the ultrathin glass were attached onto the LED device in alignment with the UV LED chips. Each pixel of the polarized light devices was controlled by a microcontroller unit (MCU). All LED programming was based on the C++ language.

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List of Changes

The changes are listed in order of appearance in the manuscript and Supplementary Information. The new text in the manuscript is indicated in yellow, and the new text in the Supplementary Information is indicated in blue. Page and line are counted based on the revised manuscript.

Revised texts in Manuscript

Discussions were revised and added to the manuscript: page 7 line 3 ~ line 7; page 7 line 7 ~ line 9; page 7 line 34 ~ page 8 line 3; page 8 line 3 ~ line 5; page 8 line 8 ~ line 11; page 8 line 33 ~ page 9 line 2; page 9 line 4 ~ line 6; page 9 line 6 ~ line 13.

Methods were revised and added for detailed information: page 24 line 11 ~ 13; page 24 line 16 ~ line 18; page 25 line 13 ~ 26.

Corrections in the manuscript were made: page 5 line 2; page 6 line 22; page 8 line 7 and 8; page 9 line 2; page 12 line 4; page 19 line 29 ~ page 21 line 28; page 26 line 11 and 13.

The Acknowledgments were modified: page 18 line 6.

Revised figures in Manuscript

Correction in figure label and caption were made: Figure 1b; Figure 2e.

Revised texts and figures in Supplementary Information

New figures and captions were added to the supplementary information: Figure S5, Figure S10, Figure S12, Figure S13, Figure S17, Figure S18, Figure S19, Figure S20,

Corrections in the supplementary information were made: page 35 line 2 ~ page 36 line 16.

References 7 were added.

REVIEWERS' COMMENTS

Reviewer #3 (Remarks to the Author):

The authors have addressed all of my concerns. I can now recommend the publication of this work.

Reviewer #4 (Remarks to the Author):

I am satisfied with the authors' revisions to the article and agree to its publication.