Reversible phase transition for switchable second harmonic generation in 2D perovskite microwires

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Abstract
Highly efficient second-harmonic generation (SHG) has facilitated the development of nanophotonics and sustained promising applications, ranging from electro-optical modulation, frequency conversion, and optical frequency combs to pulse characterization. Although controllable SHG switching has been observed in nanophotonics structures and molecule systems, the relatively small SHG switching contrast impedes its application in switchable nonlinear optics. Herein, reversible phase transitions between glassy and crystalline states without material degradation are demonstrated based on solution-processed chiral perovskite microwire arrays. Breaking of lattice inversion symmetry and high crystallinity support efficient SHG in microwire arrays. By synergy of high-performance SHG and reversible phase transitions between glassy and crystalline states, reversible switching of SHG is demonstrated under facile conditions. The high SHG switching performances, together with a small footprint, pave the way toward the integration of switchable nonlinear devices based on microwire arrays.

KEYWORDS
2D chiral perovskites, assembled microwires, nonlinear optics, phase transition, second harmonic generation
1 | INTRODUCTION

Second-harmonic generation (SHG) is a nonlinear optical process that enables converting two identical low-frequency photons into one photon with twice frequency, which boosts the development of optoelectronics, ranging from electro-optical modulation, frequency conversion, and optical frequency combs to pulse characterization.\(^1\)–\(^4\) In particular, the modulation of the SHG signal such as SHG switching presents promising applications, which extend the versatility of modern photonic applications toward computation, optical communication, data security, and optical switching. The realization of SHG switching relies on nanophotonic systems by applying strain, light, and electric fields.\(^5\)–\(^12\) The complexity and high cost of nanophotonics processing, fabricated by chemical vapor deposition and electron-beam lithography techniques, hinder the broad applications of SHG switching. In contrast, low-cost solution-processable semiconductors with stimuli-responsive properties offer a feasible approach to constructing reversible solid-state SHG switching, but the fabrication of large SHG switching contrast is still challenging.\(^13\)–\(^18\) Based on the single crystallinity of self-assembled CsPbBr\(_3\) perovskite microwires, Xiong and his colleagues\(^19\) demonstrate all-optical switching on a picosecond time scale.

Layered metal-halide perovskites, a typical solution-processable semiconductor, have stimulated great interest due to their optoelectronic properties.\(^20\)–\(^32\) The crystal structure constructed by conductive octahedron frameworks and insulating intercalated bulky cations endows layered perovskite with semiconducting properties and exotic properties, such as SHG,\(^33\)–\(^35\) ferroelectricity,\(^36\) spin polarization,\(^37\) bulk photovoltaic effect,\(^38\) circular dichroism,\(^39\)\(^40\) and Rashba-Dresselhaus spin–orbit coupling.\(^41\) Recently, SHG has been demonstrated based on layered perovskites, which can be attributed to the insertion of bulky cations for breaking the lattice symmetry of perovskite.\(^34\)\(^42\) Based on reversible ferroelectric to paraelectric phase transitions, the SHG switching corresponding to a room-temperature high-SHG state and a high-temperature low-SHG state has also been reported, but this switching process cannot be maintained at mild temperature due to the instantaneous reversal from paraelectric to ferroelectric phase upon temperature removal, thus hampering their practical applications.\(^35\) Therefore, the controlled phase changes in layered perovskite crystals are critical for the realization of SHG switching. Besides the difficulty of preparing SHG switching under facile conditions, it is still challenging for the patterning of layered perovskites into integrated nonlinear devices.

Here, we realize switchable SHG on the basis of reversible phase transition between glassy and crystalline states in two-dimensional (2D) chiral perovskite microwire arrays. After multiple phase transitions, no morphological damage and thermal degradation are observed by temperature-dependent X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM). Based on the enhanced crystallinity of chiral microwire arrays with pure crystallographic orientation, higher SHG performance is realized compared to the perovskite films. Integrating high-performance SHG with reversible phase transitions, durable SHG switching is demonstrated without degradation by periodically alternating glassy and crystalline states. Our results open new opportunities for the integration of switchable nonlinear devices with high SHG switching performances.

2 | EXPERIMENTAL SECTION

2.1 | Fabrication of (R/S/rac-NPB)\(_2\)PbBr\(_4\) perovskite microwire arrays by a capillary-bridge assembly strategy

To prepare the precursor solutions, 40 mg synthesized perovskite powders were dissolved in 1 ml dimethylsulfoxide (DMSO). Then, a 5 \(\mu\)l precursor solution was dropped onto the asymmetric-wettability topographical template followed by covering with a target substrate. The assembly system was placed in a vacuum oven at 70°C for 12 h. Finally, regular perovskite single-crystalline microwire arrays were obtained after the complete evaporation of the solvent.

2.2 | Characterizations

The crystal structures of powders and microwire arrays were collected by an X-ray diffractometer (Bruker, D8 focus) equipped with monochromatized Cu K\(_\alpha\) radiation (\(\lambda = 1.5406\) Å). HR-XRD and temperature-dependent XRD patterns were measured by an X-ray high-resolution diffraction system (Rigaku Corporation). The morphologies of microwire arrays were acquired by SEM (Hitachi, S-4800) operating at a 5 kV voltage. The topography, height diagram, and surface potential of the microwire arrays were collected by AFM (Bruker, Dimension FastscanBio). \(\phi = \phi_{\text{tip}} - \phi_{\text{ref}}\), where \(\phi\), \(\phi_{\text{tip}}\), and \(\phi_{\text{ref}}\) are the measured potential, tip potential, and sample potential, respectively. The in-situ fluorescent photographs were acquired by an optical microscope equipped with a charge-coupled device camera. The chemical
composition of perovskite microwire arrays was measured using XPS (Thermo Scientific, ESCALAB 250Xi). The optical absorption was measured by a UV-vis-NIR spectrophotometer (Agilent, Cary 7000). The PL spectra were collected using a microscopic confocal laser Raman spectrometer (Renishaw, inVia-Qantor). The CD spectra were measured by a circular dichroism spectrometer (JASCO, J-815). TEM and SAED patterns were collected by a transmission electron microscope (2100; JEOL). The grazing-incidence wide-angle X-ray scattering (GIWAXS) images were acquired by the Beijing Synchrotron Radiation Facility. DSC and TGA were performed by a thermogravimetric differential thermal analyzer (Netzsch, STA 449F3). Measurement of nonlinear optics was performed by a home-built confocal microscope equipped with a femtosecond pulsed laser. The currents of memory devices were measured by a Keithley 4200 semiconductor characterization system equipped with a manual probe station (Lake Shore) under vacuum of $10^{-5}$ torr at room temperature.

3 RESULTS AND DISCUSSIONS

For the fabrication of 1D chiral perovskite microwire arrays, bulk crystals were obtained by incorporating the bulky chiral cations of 1-(1-naphthyl)ethylamine into the layered perovskite lattice (material synthesis can be found in Supporting Information: Note S1). Perovskite powders with left-hand, right-hand, and racemic cations are termed as (R-NPB)$_2$PbBr$_4$, (S-NPB)$_2$PbBr$_4$, and (rac-NPB)$_2$PbBr$_4$, respectively. The phase purity of perovskite powders was solidly verified by XRD (Supporting Information: Figure S1). The chiral perovskite crystal structures and organic cations are depicted in Supporting Information: Figure S1. The chiral perovskite crystalline structures and organic cations were shown in Supporting Information: Figure S2, showing the mirror-plane relationship between (R-NPB)$_2$PbBr$_4$ and (S-NPB)$_2$PbBr$_4$ perovskite crystals. Compared to the centrosymmetric $P_{21/c}$ space group of (rac-NPB)$_2$PbBr$_4$ perovskite, both (R-NPB)$_2$PbBr$_4$ and (S-NPB)$_2$PbBr$_4$ perovskites crystallize in the noncentrosymmetric polar $P_2_1$, space group due to the introduction of the chiral cations, which is crucial for the SHG. To verify the phase transition behaviors of chiral perovskite, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed. An endothermic peak at 175.93°C is revealed for (R-NPB)$_2$PbBr$_4$ perovskite during the heating runs, indicating the occurrence of melt phase transition (Supporting Information: Figure S3A). After cooling to room temperature, the glassy state is still retained and can be reversibly transformed into crystals by reheating above the crystallization temperature (Supporting Information: Figure S3B). The exceptionally low melting temperature ensures that the perovskite does not decompose during the phase-change process, which facilitates the preparation of functionalized devices. Compared to the (R-NPB)$_2$PbBr$_4$ perovskite, a dramatically higher melting temperature for (rac-NPB)$_2$PbBr$_4$ perovskite is revealed during the heating runs, which can be attributed to different hydrogen bonding and packing characteristics (Supporting Information: Figure S4). Supporting Information: Figure S5 shows morphology and fluorescence changes of perovskite powders in crystalline and glassy states. The warm-white fluorescence for crystalline-state perovskite can be attributed to self-trapped state emission. X-ray photoelectron spectroscopy (XPS) was employed to study the composition of the glassy and crystalline states. The characteristic peaks of Pb$^{4+}$ do not change after the crystal–glass phase transition, implying that the presence of PbBr$_6^{4-}$ octahedra in the glassy state; on the contrary, the binding energy position of N$_{1s}$ shifts to a smaller value, due to the change of position within the crystal structure (Supporting Information: Figure S6).

To fabricate layered perovskite microwire arrays, a capillary-bridge assembly strategy was employed to regulate the liquid distribution and directional mass transportation by introducing an asymmetric-wettability topographical template with lyophilic tops and lyophobic sidewalls (Supporting Information: Figure S7). After the complete total evaporation of the solvent, large-scale layered perovskite microwire arrays with the precise position and strict alignment were formed onto the target substrate (Figure 1A). The assembled microwire arrays present the blue fluorescence in accordance with the perovskite powder in glassy states (Figure 1B). No diffraction spots were further determined by the XRD and GIWAXS, indicating the nature of the amorphous state, which can be attributed to the large size and hydrogen bonding of the chiral spacer cations impeding its crystallization during the evaporation of the solvent (Figure 1E and Supporting Information: Figure S8). Under in situ fluorescence microscopy, the appearance of warm-white fluorescence demonstrates the nucleation of layered perovskite microwire arrays when the temperature exceeds the crystallization temperature (Figure 1C). Crystallinity and crystallographic orientation of perovskite microwire arrays were confirmed by GIWAXS. As shown in Figure 1F, the discrete Bragg diffraction spots indicate that the initial nucleation within microwire arrays presents a strict crystallographic orientation. By further increasing the temperature of the substrate, the fluorescence of microwire arrays completely changes to warm-white fluorescence, suggesting complete crystallization (Figure 1D). Crystallinity and crystallographic orientation corresponding to this stage were also...
demonstrated by the GIWAXS. The discrete Bragg diffraction spots with enhanced intensity indicate the formation of pure (001)-oriented perovskite microwire arrays with high crystallinity (Figure 1G).

To rigorously investigate the evolution of crystallography, spectroscopy, and morphology for microwire arrays during the phase transition, temperature-dependent XRD, ultraviolet-visible (UV-vis) spectroscopy, AFM, and SEM were carried out. As shown in Figure 2A and Supporting Information: Figure S9, diffraction peaks located at 4.6° corresponding to the (001) crystal planes appear when the temperature reaches 90°C, indicating the beginning of crystallization. As the temperature increases, the diffraction peak intensity reaches its maximum value and then starts to
decrease. Meanwhile, the diffraction peak shifts to a smaller value accompanied by the elevated temperature due to the growth of the perovskite grain (Figure 2B). The variation of the diffraction peaks intensity extracted from (001) and (002) crystal planes is shown in Figure 2C. The temperature-dependent absorption spectra of microwires were also carried out. The absorption peak eventually shifts to 390 nm wavelength corresponding to the exciton resonance peak of the crystalline perovskite with the increased temperature (Supporting Information: Figure S10). As shown in Figure 2D–I, no significant morphological difference can be distinguished among the glassy and crystalline microwire arrays, but there is a large difference in fluorescence images and surface potential. To evaluate the thermal stability of (R/S-NPB)$_2$PbBr$_4$ microwire arrays, multiple cycling experiments were performed by periodically alternating glassy and crystalline states. As shown in Figure 2J and Supporting Information: Figure S11, no obvious degradation occurs after multiple phase transitions, indicating the excellent thermal durability of perovskite microwire arrays.

To characterize the morphology and surface roughness of the crystalline perovskite microwire arrays, SEM and AFM were performed. SEM images illustrate strict alignment, homogeneous size, and precise position of microwire arrays (Supporting Information: Figure S12). Zoom-in SEM image reveals the smooth surfaces and straight edge of a single microwire. A smooth surface with a height of about 200 nm and a width of about 4 μm is further demonstrated by the AFM image (Supporting Information: Figure S13). Furthermore, we investigated UV-vis absorption, photoluminescence (PL), and circular dichroism (CD) spectra to study the optical properties of (R/S/rac-NPB)$_2$PbBr$_4$ microwire arrays. As shown in Figure S14, the same exciton resonance peak centered at 390 nm is revealed for (R/S/rac-NPB)$_2$PbBr$_4$ microwire arrays. The PL spectra present a weak exciton emission.
peak accompanied by a strong self-trapped exciton emission ranging from 500 to 700 nm, resulting in the warm-white fluorescence of microwire arrays (Supporting Information: Figure S15). As shown in Supporting Information: Figure S16, the bisignated CD absorption peaks of (R/S-NPB)\textsubscript{2}PbBr\textsubscript{4} microwire arrays are observed at the same peak position but with opposite signal, indicating that the chirality of organic cations has been successfully transferred to the inorganic perovskite layers. In contrast, no absorption difference is found for (rac-NPB)\textsubscript{2}PbBr\textsubscript{4} microwire arrays due to the racemic blend nature.

To characterize the crystallinity and crystallographic orientation of the crystalline perovskite microwire arrays, XRD, high-resolution XRD (HR-XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and GIWAXS were performed. As shown in Figure 3A, (R/S/rac-NPB)\textsubscript{2}PbBr\textsubscript{4} microwire arrays all exhibit periodic diffraction peaks, indexed to (00k) planes, indicating the pure crystallographic orientation. The narrow full width at half-maximum of about 0.070° was demonstrated by HR-XRD, revealing the excellent crystallinity of perovskite microwire arrays (Figure 3B). The smooth surface and sharp edge of (R-NPB)\textsubscript{2}PbBr\textsubscript{4} microwire are illustrated by the TEM pattern. The SAED image presents sharp diffraction spots, indicating the single crystallinity of perovskite microwires with preferential growth along the (010) direction (Figure 3C,D). The preferential crystallographic orientations of (R/S/rac-NPB)\textsubscript{2}PbBr\textsubscript{4} microwire arrays were further demonstrated by GIWAXS (Figure 3E-G). The sharp and discrete Bragg diffraction spots demonstrate excellent crystallinity of perovskite microwire arrays with pure (001) crystallographic orientation. In addition, the XRD shows no appreciable degradation after exposure to the ambient condition for 30 days, indicating the excellent long-term stability of chiral perovskite microwire arrays (Supporting Information: Figure S17).

Breaking the symmetry of a crystal structure is indispensable for SHG activity. Considering that (R/S-NPB)\textsubscript{2}PbBr\textsubscript{4} chiral perovskite crystallizes in the noncentrosymmetric polar space group $P\textsubscript{2}1\textsubscript{1}$, it is considered to be an SHG-active material. Figure 4A shows the schematic

![Figure 3](https://example.com/figure3.png)

**Figure 3** Crystallographic characteristics of chiral single-crystalline microwire arrays. (A) XRD pattern and (B) the rocking curves of perovskite microwire arrays. (C) TEM image and (D) SAED pattern of a perovskite microwire, revealing excellent crystallinity with preferential growth along the (010) direction. GIWAXS patterns of (E) (R-NPB)\textsubscript{2}PbBr\textsubscript{4}, (F) (S-NPB)\textsubscript{2}PbBr\textsubscript{4}, and (G) (rac-NPB)\textsubscript{2}PbBr\textsubscript{4} microwire arrays, revealing (001)-oriented microwire arrays. Scale bar, 4 μm. GIWAXS, grazing-incidence wide-angle X-ray scattering; SAED, selected area electron diffraction; TEM, transmission electron microscopy; XRD, X-ray diffraction.
illustration of SHG characterization consisting of a femtosecond pulsed laser, a half-wave plate (HWP), mirrors, an attenuator plate, a detector, and perovskite microwire arrays. To estimate the nonlinear-optical (NLO) coefficients of chiral perovskite, particle size-dependent SHG characterization was carried out using a 1064 nm laser irradiation. As shown in Supporting Information: Figure S18, with the particle size increasing, the SHG intensities increase and gradually reach the maximum, indicating a phase-matching behavior of (R/S-NPB)$_2$PbBr$_4$ perovskites. The SHG intensities of chiral perovskite are about 0.68 times that of the KDP. Figure 4B,C shows the power-dependent SHG measurement under an 800 nm laser irradiation. The quadratic dependence of the SHG intensities with the laser power indicates the SHG energy conversion relationship for (R/S-NPB)$_2$PbBr$_4$ perovskite microwire arrays. In contrast, no detectable SHG signals were found for (rac-NPB)$_2$PbBr$_4$ perovskite microwire arrays because of the centrosymmetric space group $P_{21/c}$ (Supporting Information: Figure S19). The wavelength-dependent SHG spectra of (R-NPB)$_2$PbBr$_4$ perovskite microwire arrays were investigated at different excitation wavelengths ranging from 740 to 850 nm with a step of 10 nm under a fixed irradiation power of 8 mW (Figure 4D). The extracted SHG intensity from different excitation wavelengths is shown in Figure 4E. The polarization-dependent SHG intensity from (R-NPB)$_2$PbBr$_4$ microwire arrays is obtained by rotating the HWP under an 800 nm laser irradiation. The typical angle-dependent SHG intensity of (R-NPB)$_2$PbBr$_4$ microwire arrays at different polarization angles with a fixed illumination power of 8 mW is displayed in Figure 4F, showing clear angular dependence. The 0° polarization is defined as the axial direction of the microwire arrays. With the rotation of the incident laser polarization from 0 to 180° with an angle interval of 10°, the SHG intensity exhibits a maximum at 0° when the polarization is parallel to the microwire arrays and a minimum at 90° when the polarization is perpendicular to the microwire arrays. As the polarization angle gradually
increases from 90 to 180°, the SHG intensity reaches a maximum again at 180°, suggesting excellent SHG performance due to the single crystallinity and pure crystallographic orientation of microwire arrays. The SHG polarization ratio, defined as $I_{\text{max}}/I_{\text{min}}$, is calculated by extracting the SHG intensity maximum (minimum) value at the polarization of 0° (90°). The calculated SHG anisotropy ratio is 23.1 for (R-NPB)$_2$PbBr$_4$ microwire arrays (Supporting Information: Figure S20). The excellent SHG performance was also demonstrated for (S-NPB)$_2$PbBr$_4$ microwire arrays (Supporting Information: Figure S21). Furthermore, we carried out control experiments by measuring SHG based on spin-coated thin films to verify higher SHG conversion efficiency based on high-quality microwire arrays. Compared to microwire arrays, spin-coated thin films present weaker SHG intensity under the same illumination power, which can be attributed to a large number of grain boundaries and surface traps yielding lower crystallinity (Supporting Information: Figures S22 and S23). These results demonstrate that the microwire arrays with enhanced crystallinity and pure crystallographic orientation significantly enhance the SHG performance.

Given that the perovskite microwires enable reversible phase transitions between glassy and crystalline states, we sought to demonstrate switchable SHG using (R/S-NPB)$_2$PbBr$_4$ microwire arrays. No SHG signal was found for glassy-state (R/S-NPB)$_2$PbBr$_4$ perovskite microwire arrays because of the short-range order and isotropic structure (Supporting Information: Figure S24). Figure 5A,D shows the temperature-dependent SHG intensity under an 800 nm laser irradiation with a fixed illumination power of 8 mW. The SHG intensity increases rapidly with the elevated temperature from 90 to 140°C, which can be attributed to the transition from the glassy to the crystalline state, which is consistent with the temperature-dependent XRD. To verify the effect of the phase transition on the SHG signal, three thermal cycles and recorded SHG intensity were measured. Crystalline (R/S-NPB)$_2$PbBr$_4$ perovskite microwire arrays display strong SHG responses, whereas the SHG signals fall directly to zero for the glassy state. No appreciable attenuation was found after several phase transitions, suggesting extremely stable thermal properties of perovskite microwire arrays.

**Figure 5** Durable SHG switching of perovskite microwire arrays. Temperature-dependent SHG intensities of (A) (R-NPB)$_2$PbBr$_4$, and (D) (S-NPB)$_2$PbBr$_4$ perovskite microwire arrays under an 800 nm laser illumination. Stability tests of SHG intensity for (B) (R-NPB)$_2$PbBr$_4$, and (E) (S-NPB)$_2$PbBr$_4$ perovskite microwire arrays between amorphous and crystalline states, demonstrating extremely stable thermal properties of perovskite microwire arrays. Reversible SHG switching between amorphous and crystalline states for (C) (R-NPB)$_2$PbBr$_4$, and (F) (S-NPB)$_2$PbBr$_4$ perovskite microwire arrays. SHG, second-harmonic generation.
arrays (Figure 5B,E). A combination of reversible phase transitions and high-performance SHG, switchable SHG is realized by alternating glassy and crystalline states based (R/S-NPB)$_2$PbBr$_4$ perovskite microwire arrays (Figure 5C,F). Furthermore, representative phase-change memory devices constructed by microwire arrays are also demonstrated based on the phase transitions. Compared to the devices in the glassy state, the higher dark currents with nearly two orders of magnitude are revealed for the devices in the crystalline state. Reversible current switching between glassy and crystalline states is also demonstrated without appreciable attenuation after 30 cycles, greatly satisfying the requirements of memory devices (Supporting Information: Figure S25).

4 CONCLUSIONS

In conclusion, reversible phase transitions between glassy and crystalline states without degradation are demonstrated based on chiral layered perovskite microwire arrays, which can be attributed to the change of perovskite crystallization kinetics due to the insertion of chiral bulky cations. The symmetry breaking of the layered perovskite structure underpins the realization of SHG. Combining high-performance SHG with reversible phase transitions, efficient SHG switching with ultra-long durability is demonstrated by alternating glassy and crystalline states under feasible conditions. The high SHG switching performances, together with the high-throughput solution-processing assembly techniques, highlight promising applications for the on-chip integration of nonlinear photonic devices based on microwire arrays.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supplementary material of this article.

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**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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