

# Optical Properties of a CsMnBr<sub>3</sub> Single Crystal

Yingzhuang Xu, Junzi Li, Fuli Zhao, Yang Gao,\* Rui Chen, and Tingchao He

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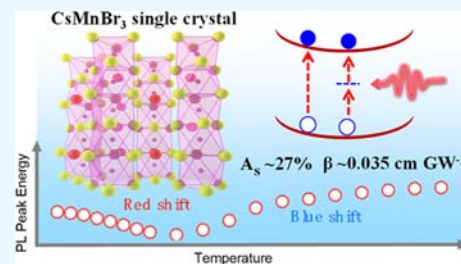


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**ABSTRACT:** Lead-free perovskite materials with good stability are promising for various applications. In order to explore their application in optoelectronic devices, it is essential to investigate their fundamental optical properties. In this work, we have synthesized a CsMnBr<sub>3</sub> single crystal (SC) with red emission at ~621 nm and studied their optical properties. Through the measurement of temperature-dependent photoluminescence (PL) spectra, it is found that a phase transition occurs at approximately 100 K in the SC, which is absent in the CsMnBr<sub>3</sub> nanocrystals (NCs). Furthermore, the SC exhibits stronger electron and longitudinal optical phonon coupling strength than that of the NCs at low temperatures. In addition, under the resonant excitation at 600 nm, the SC possesses strong saturable absorption property, with a modulation depth of ~27%. Interestingly, the SC also exhibits a large two-photon absorption coefficient of ~0.035 cm GW<sup>-1</sup> at 800 nm and an excellent optical limiting behavior. The experimental results indicate that the CsMnBr<sub>3</sub> SC is a class of excellent environmentally friendly optoelectronic materials.



## INTRODUCTION

All inorganic perovskite materials (CsPbX<sub>3</sub>, X = Cl, Br, and I) have been widely used in various applications, such as light detection, photovoltaic cell, and laser, because of their excellent optoelectronic properties, including high photoluminescence quantum yield (PLQY), widely tunable PL emission, and large absorption cross section.<sup>1</sup> However, the intrinsic toxicity of these materials greatly hinders their practical applications. Therefore, to reduce the toxicity of the materials, researchers have synthesized various lead-free perovskite materials, with Cu<sup>2+</sup>, Sn<sup>2+</sup>, and Bi<sup>3+</sup> as substitutes for Pb<sup>2+</sup>,<sup>2–4</sup> and developed their application in various optoelectronic devices.

In recent years, Mn<sup>2+</sup> has been continuously studied as a dopant and an alternative element for Pb<sup>2+</sup> due to its unique luminescence,<sup>5,6</sup> which has green emission in the form of tetrahedral coordination and red emission in the form of octahedral coordination. As a newly emerging lead-free perovskite material, CsMnBr<sub>3</sub> has attracted intensive research interest.<sup>7,8</sup> However, although the research on CsMnBr<sub>3</sub> nanocrystals (NCs) is relatively adequate, CsMnBr<sub>3</sub> single crystals (SCs) have not been extensively studied. Compared with the NC counterparts, SCs are more suitable for preparing large-area optoelectronic devices.<sup>9</sup> The study on the optical properties of CsMnBr<sub>3</sub> SCs is a prerequisite for realizing their relevant application. For example, the electron–phonon coupling effect in CsMnBr<sub>3</sub> SCs can be investigated through the measurement of the temperature-dependent PL spectrum, which is crucial for developing high-efficiency photovoltaic and laser devices.<sup>10,11</sup> Investigating the nonlinear optical (NLO) behavior of CsMnBr<sub>3</sub> SCs is important to develop their applications in Q-switching and mode-locking techniques<sup>12,13</sup>

and frequency upconversion laser.<sup>14,15</sup> Nevertheless, there is still a lack of in-depth investigation on these fundamental optical properties of CsMnBr<sub>3</sub> SCs, which is unfavorable to expand their various applications.

In this work, we synthesized a CsMnBr<sub>3</sub> SC and studied its optical properties. Phase transition was observed at a temperature of approximately 100 K. In addition, it was found that the CsMnBr<sub>3</sub> SC exhibited strong saturable absorption and two-photon absorption (TPA).

## METHODS

**Sample Preparation.** The CsMnBr<sub>3</sub> SC was obtained through a slow evaporation method described in the previous literature.<sup>7</sup> Briefly, 0.55 mmol CsBr and 1 mmol MnBr<sub>2</sub> were added to the mixed solution of water and hydrobromic acid (19:1 in weight) and then heated to 40 °C in ambient conditions. As a result, the CsMnBr<sub>3</sub> SC with a size in millimeter level was formed after storage for 5 days. CsMnBr<sub>3</sub> NCs were prepared through a hot-injection method according to a previous procedure with a slight modification.<sup>8</sup> During the synthesis process, 1-octadecene was used as a solvent, while oleic acid and oleylamine were used as ligands. The trimethylbromosilane precursor was rapidly injected into the solution of cesium acetate and manganese acetate precursor at 170 °C. After reaction for 20 s, an ice–water bath was used to

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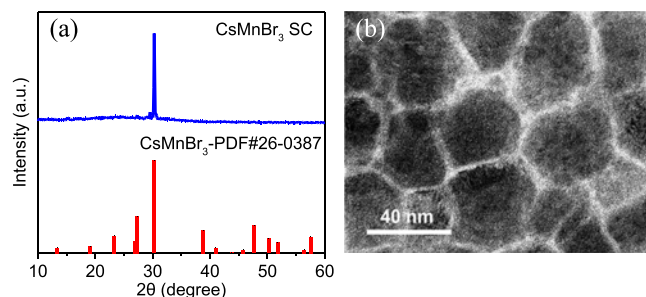
put out the reaction. CsMnBr<sub>3</sub> NCs were then obtained by a centrifugation method.

**Characterization.** The crystal structure of the CsMnBr<sub>3</sub> SC was determined by using X-ray diffraction (XRD, I scalab 250Xi), while the morphology of NCs was analyzed by using transmission electron microscopy (TEM, JI M-2100F). Excitation and PL spectra and lifetimes were recorded by an Edinburgh F55 spectrometer. PLQYs were obtained using an F55 fluorescence spectrometer with an integrating sphere. The temperature-dependent PL spectra were collected from 10 to 300 K, which was excited by an He–Cd laser at 442 nm.

**NLO Measurements.** Our home-built microregion NLO system was used to investigate the NLO properties of CsMnBr<sub>3</sub> SC. The fs pulses at 600 and 800 nm output from TOPAS (Spectra-Physics, 1000 Hz, 100 fs) were used as resonant and nonresonant excitation sources, respectively. The PL spectra under 800 nm excitation were collected by a 20× objective lens (NA = 0.45) and then detected by the charged coupling device (SpectraPro HHS-300). The TPA coefficient of CsMnBr<sub>3</sub> SC was determined using the nonlinear transmittance method.<sup>16</sup>

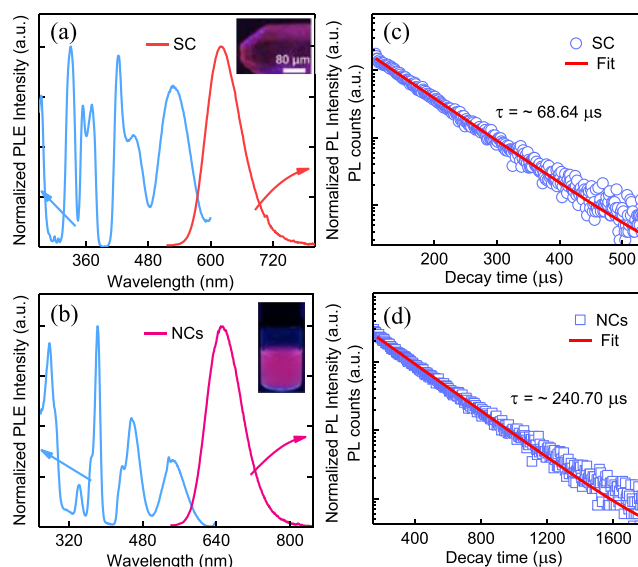
## RESULTS AND DISCUSSION

The XRD pattern of CsMnBr<sub>3</sub> SC is depicted in Figure 1a, which reveals its hexagonal crystal structure.<sup>17</sup> The TEM image



**Figure 1.** (a) XRD pattern of CsMnBr<sub>3</sub> SC. (b) TEM image of CsMnBr<sub>3</sub> NCs.

of CsMnBr<sub>3</sub> NCs confirms their hexagonal morphology (Figure 1b). Under the excitation of 278 nm, both CsMnBr<sub>3</sub> SC and NCs exhibit red emission, with their PL spectra peaking at ~621 and ~653 nm, respectively (Figure 2a,b). The PLQYs of CsMnBr<sub>3</sub> SC and NCs were determined as 26 and 53%, respectively. Although both the samples possess multiple peaks in the PL excitation spectra, only a single PL peak was observed. In addition, we measured excitation-wavelength-dependent PL spectra of the SC and NCs (Figure S1). It was found that the PL peaks of the two samples did not change at different excitation wavelengths, indicating that the same emissive states were involved for both of them. The PL emission for both the CsMnBr<sub>3</sub> SC and NCs was ascribed to the transition from <sup>4</sup>T<sub>1</sub> to the ground state <sup>6</sup>A<sub>1</sub>.<sup>7</sup> It was found that the CsMnBr<sub>3</sub> SC still exhibited bright red emission even when it was kept at about 35% humidity for over 6 months. The time-resolved PL decay curves of CsMnBr<sub>3</sub> SC and NCs were measured at 300 K under the excitation of 422 nm (Figure 2c,d), determining their lifetimes as ~68.64 and ~240.70 μs through the monoexponential fitting. Because more defects were formed in the SC and the surface defects on the CsMnBr<sub>3</sub> NCs can be effectively passivated by the ligands, the PL lifetime of the former is much shorter than that of the



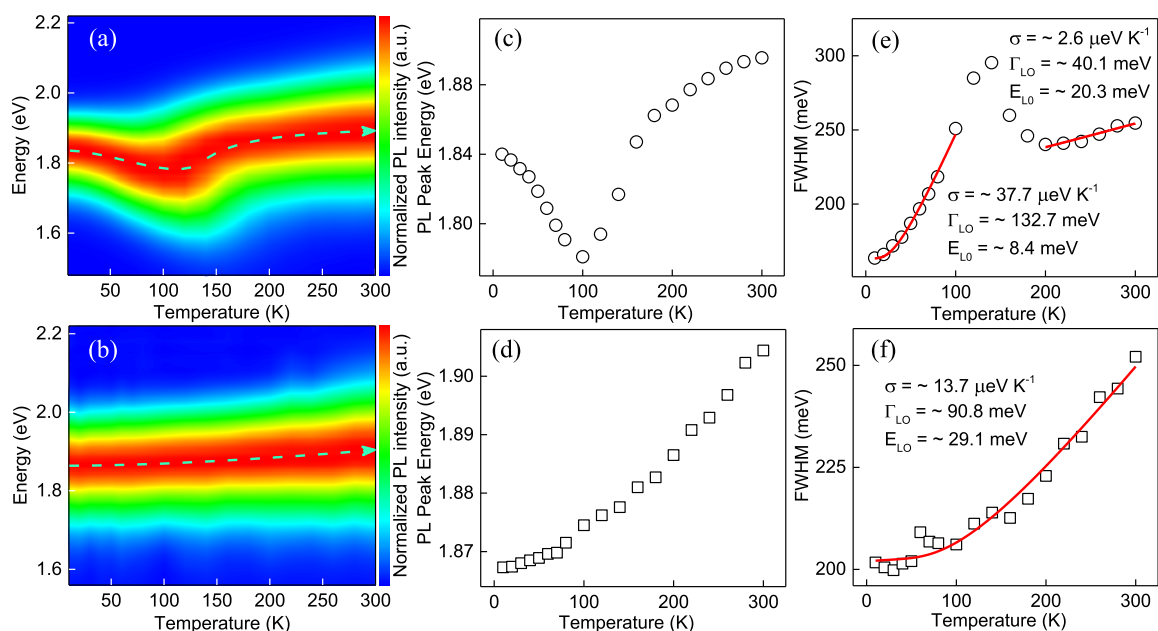
**Figure 2.** (a,b) Excitation and emission spectra of CsMnBr<sub>3</sub> SC and NCs. Insets: their photographs under UV light irradiation. (c,d) Time-resolved PL decay curves of CsMnBr<sub>3</sub> SC and NCs.

latter. It should be noted that the PL lifetime in our CsMnBr<sub>3</sub> NCs was much different from those in previous literature, which should be caused by the different local structures around Mn ions.<sup>7,8</sup>

To analyze the low-temperature optical properties of CsMnBr<sub>3</sub> SC, its PL spectra were measured as a function of temperature ranging from 10 to 300 K by using a 442 nm He–Cd laser as the excitation source (Figure 3a,b). As depicted in Figure 3c, as the temperature increases from 10 to 100 K, the PL peak of CsMnBr<sub>3</sub> SC exhibits a bathochromic shift. However, a blue shift of the PL peak was observed from 100 to 300 K. The sudden change of the PL peak energy at approximately 100 K should be associated with the occurrence of phase transition. Although the phase transition was reported in other relatively soft materials, such as the MAPbI<sub>3</sub> bulk film,<sup>18</sup> this is the first time that the phase transition was observed in the CsMnBr<sub>3</sub> SC. More experimental investigation was needed to further confirm the mechanism for the occurrence of phase transition in the SC.

In contrast, the PL peak of CsMnBr<sub>3</sub> NCs exhibited a monotonous blue shift with increasing temperature (Figure 3d), indicating the absence of phase transition. Actually, previous literature implied that colloidal NCs generally exhibit better thermodynamic phase stability than bulk materials, which was caused by the reduced crystal-field strength and smaller splitting energy of the excited state during thermal expansion.<sup>8,19</sup> Compared with the SC, the better phase stability of CsMnBr<sub>3</sub> NCs should be caused by the ligand-induced change in surface energy. Actually, such kind of stabilization phenomenon was also reported in CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and FAPbI<sub>3</sub> that were modified by appropriate ligands.<sup>20,21</sup> Therefore, the phase transition observed in the CsMnBr<sub>3</sub> SC may be ascribed to the absence of the ligand-induced phase stabilization effect.

The change of full width at half-maximum (fwhm) of the PL spectrum is correlated with electron-phonon coupling.<sup>22</sup> Such an effect has been widely investigated through the measurement of temperature-dependent PL fwhm in Mn-doped perovskite NCs,<sup>23</sup> but it has never been reported for the CsMnBr<sub>3</sub> SC. Therefore, the PL fwhm of the CsMnBr<sub>3</sub> SC and



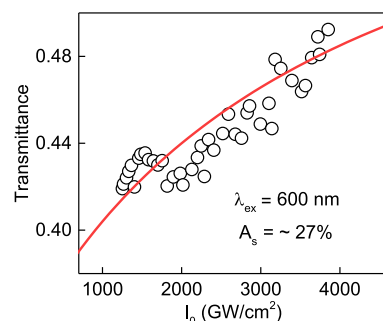
**Figure 3.** Pseudo-color maps of the temperature-dependent PL spectra of (a) CsMnBr<sub>3</sub> SC and (b) CsMnBr<sub>3</sub> NCs. PL peak energy and fwhm as a function of temperature for (c,e) CsMnBr<sub>3</sub> SC and (d,f) CsMnBr<sub>3</sub> NCs.

NCs at different temperatures was analyzed. As shown in Figure 3e, the PL fwhm of the CsMnBr<sub>3</sub> SC broadens at temperatures ranging from 10 to 140 and 200 to 300 K. In contrast, the PL fwhm decreases between 140 and 200 K, probably caused by the occurrence of phase transition. As expected, the PL fwhm of CsMnBr<sub>3</sub> NCs broadens monotonously as the temperature increases from 10 to 300 K (Figure 3f), which is similar to those of CsPbX<sub>3</sub> (X = Cl, Br, and I) NCs.<sup>24</sup> The PL fwhm as a function of temperature can be expressed as<sup>25,26</sup>

$$\Gamma(T) = \Gamma_{\text{inh}} + \sigma T + \Gamma_{\text{LO}} / [\exp(E_{\text{LO}}/k_{\text{B}}T) - 1] \quad (1)$$

where  $\Gamma_{\text{inh}}$  is the inhomogeneous broadening term,  $\sigma$  is the coupling coefficient of electron and acoustic phonon,  $\Gamma_{\text{LO}}$  is the coupling strength between the electron and longitudinal optical (LO) phonon, and  $E_{\text{LO}}$  is the LO phonon energy. Through theoretical fitting, for the SC at 10–100 K,  $\sigma$  is  $\sim 37.7 \mu\text{eV K}^{-1}$ , while  $\Gamma_{\text{LO}}$  and  $E_{\text{LO}}$  are  $\sim 132.7$  and  $\sim 8.4$  meV, respectively. At 200–300 K,  $\sigma$  is  $\sim 2.6 \mu\text{eV K}^{-1}$ , while  $\Gamma_{\text{LO}}$  and  $E_{\text{LO}}$  are  $\sim 40.1$  and  $\sim 20.3$  meV, respectively. For the CsMnBr<sub>3</sub> NCs, during the whole measured temperature range,  $\sigma$  is  $\sim 13.7 \mu\text{eV K}^{-1}$ , and  $\Gamma_{\text{LO}}$  and  $E_{\text{LO}}$  are  $\sim 90.8$  and  $\sim 29.1$  meV, respectively. Compared with CsMnBr<sub>3</sub> NCs, the SC has stronger electron and LO phonon coupling strength at low temperatures but weaker coupling strength at high temperatures.

Next, the NLO properties of the CsMnBr<sub>3</sub> SC and NCs were comparatively investigated under resonant and non-resonant excitation (600 and 800 nm). However, no obvious NLO signals were detected in the NCs under the excitation of above two wavelengths, probably caused by the low concentration of CsMnBr<sub>3</sub> NCs ( $1 \times 10^{-5}$  M). Considering that the SC has more advantages in the practical application of optoelectronic devices, only the NLO properties of CsMnBr<sub>3</sub> SC were studied in the following discussions. Under the resonant excitation at 600 nm, it was found that the transmittance of the CsMnBr<sub>3</sub> SC increased with increasing excitation intensity (Figure 4), confirming the occurrence of



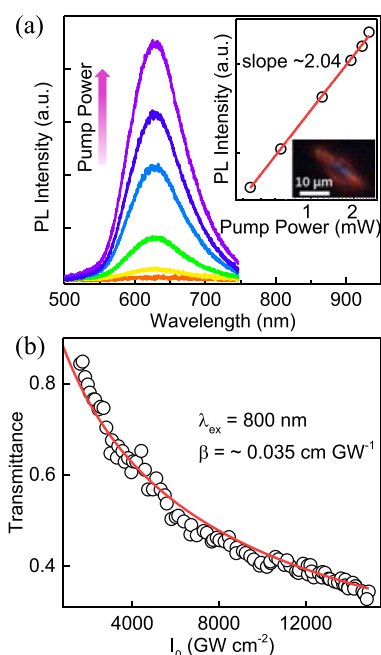
**Figure 4.** Excitation intensity-dependent transmittance of the CsMnBr<sub>3</sub> SC and the corresponding theoretical fitted curve under the excitation at 600 nm (100 fs, 1000 Hz).

saturable absorption. The excitation intensity-dependent transmittance of the sample can be fitted using the following formula<sup>27</sup>

$$T = 1 - A_s / (1 + I_0 / I_{\text{sat}}) - n_s \quad (2)$$

where  $A_s$  is the modulation depth,  $I_0$  is the incident intensity,  $I_{\text{sat}}$  is the saturable optical intensity that is required in a steady state to reduce the absorption to half of its unbleached value, and  $n_s$  is the non-saturable loss. Through the theoretical fitting using eq 2, the  $A_s$  value of the SC is determined as  $\sim 27\%$ , which is comparable to that of MoS<sub>2</sub> dispersion ( $\sim 34\%$ , 800 nm),<sup>28</sup> but much larger compared with the CsPbBr<sub>3</sub> NC film (13.1%, 1060 nm).<sup>29</sup> Notably, the CsMnBr<sub>3</sub> SC exhibits a high damage threshold ( $\sim 4000 \text{ GW cm}^{-2}$ ), implying that it is an excellent saturable absorber that may be used for Q-switching and mode-locking techniques.

Subsequently, the NLO behavior of the CsMnBr<sub>3</sub> SC under the non-resonant excitation was investigated. Bright PL emission peaking at  $\sim 621$  nm was easily observed under 800 nm excitation (Figure 5a). In addition, it was found that the PL intensity was proportional to the square of excitation power (inset of Figure 5a), confirming the TPA mechanism at 800 nm.<sup>30</sup> The TPA coefficient of the SC was then measured using



**Figure 5.** (a) PL spectra of the CsMnBr<sub>3</sub> SC under different excitation intensities at 800 nm (100 fs, 1000 Hz). Insets: The relationship between the PL intensity vs excitation power and the microscopic image under 800 nm excitation. (b) Transmittance under different excitation intensities and the relevant theoretical fitting curve.

the nonlinear transmittance method.<sup>16</sup> The corresponding experimental data are shown in Figure 5b, which can be fitted using the following equation

$$T(I_0) = [\ln(1 + I_0 L \beta)] / I_0 L \beta \quad (3)$$

where  $L$  is the thickness of the sample and  $\beta$  is the TPA coefficient.<sup>16</sup> Through the theoretical fitting, the  $\beta$  value of the CsMnBr<sub>3</sub> SC was determined as  $\sim 0.035 \text{ cm GW}^{-1}$ , which is 1 order of magnitude larger than that of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> SC ( $5.1 \times 10^{-3} \text{ cm GW}^{-1}$ , 600 nm),<sup>31</sup> possibly due to the larger density of states in the former. Moreover, under the excitation intensity of  $1.5 \times 10^4 \text{ GW cm}^{-2}$ , the transmittance can decrease to 34% and no obvious saturation effect was observed. It indicates that the CsMnBr<sub>3</sub> SC can be used as an excellent optical limiter, with a limiting threshold of  $\sim 0.9 \times 10^4 \text{ GW cm}^{-2}$ . It will be interesting to determine the wavelength-dependent 2PA coefficients of the CsMnBr<sub>3</sub> SC. However, we cannot obtain the 2PA coefficients at other wavelengths. In view so, the 2PA coefficient of this material was determined at the most common wavelength, that is, 800 nm, which can provide important information for the potential application in NLO devices.

## CONCLUSIONS

In conclusion, we investigated the low-temperature PL spectra and NLO properties of the CsMnBr<sub>3</sub> SC. Unlike the colloidal NC counterpart, the SC underwent a phase transition at approximately 100 K, probably due to the absence of the ligand-induced phase stabilization effect. At low temperatures, the SC exhibited stronger electron and LO phonon coupling strength than that of the NCs. Notably, the CsMnBr<sub>3</sub> SC possesses excellent saturable absorption and TPA properties, indicating that it is promising for the application in Q-

switching and mode-locking techniques and as an optical limiter.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03661>.

Excitation wavelength-dependent PL spectra of the CsMnBr<sub>3</sub> SC and NCs (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Yang Gao – Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China; [orcid.org/0000-0003-0680-4950](https://orcid.org/0000-0003-0680-4950) | email: [ygao@szu.edu.cn](mailto:ygao@szu.edu.cn)

### Authors

Yingzhuang Xu – Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

Junzi Li – Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

Fuli Zhao – Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen 518055, P. R. China

Rui Chen – Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen 518055, P. R. China; [orcid.org/0000-0002-0445-7847](https://orcid.org/0000-0002-0445-7847)

Tingchao He – Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China; [orcid.org/0000-0003-1040-0596](https://orcid.org/0000-0003-1040-0596)

Complete contact information is available at:

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## Notes

The authors declare no competing financial interest.

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